SUBSTITUTION REACTIONS OF THE AMMINE COMPLEXES OF PALLADIUM (II)

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by

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ABSTRACT

The following substitution reactions involving the square complexes of palladium (II) in aqueous HCl solution were studied by spectrophotometric and potentiometric methods:

$$Pd(NH_3)_4^{++} + H^+ + Cl^- \rightleftharpoons Pd(NH_3)_3Cl^+ + NH_4^+$$

$$Pd(NH_3)_3Cl^+ + H^+ + Cl^- \rightleftharpoons Pd(NH_3)_2Cl_2 + NH_4^+$$

Reaction rates, followed by (H^+) versus time measurements, suggest that parallel mechanisms obtain with one reaction involving the solvent as a nucleophilic reagent and a second reaction involving the incoming Cl^- reagent.

Values of the equilibrium quotients for both reactions were calculated from absorbance and pH data.

Several of the specific rate constants were calculated and a complete mechanism is proposed.

Brief studies of the trans-effect in this system and of the cis-trans isomerism of $Pd(NH_3)_2Cl_2$ are included.

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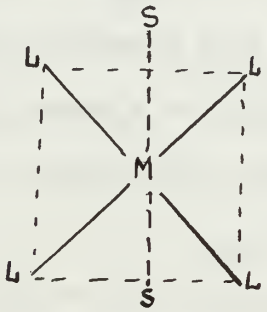
Symbol	Definition
Pd2	$Pd(NH_3)_2Cl_2$
Pd3	$Pd(NH_3)_3Cl^+$
Pd4	$Pd(NH_3)_4^{++}$
A	Absorbance
A_m	Maximum absorbance observed in absorbance versus pH plots
(H_m^+)	The hydrogen ion concentration which gives Maximum absorbance
a2	Molar extinction coef. of trans-$Pd(NH_3)_2Cl_2$
a3	Molar extinction coef. of $Pd(NH_3)_3Cl^+$
a4	Molar extinction coef. of $Pd(NH_3)_4^{++}$
$a2^*$	Molar extinction coef. of cis-$Pd(NH_3)_2Cl_2$
A_2	Minimum absorbance at low pH observed for absorbance versus pH plots
A_4	Minimum absorbance observed for high pH
D	Conversion factor determined to convert measured (H^+) to actual (H^+)
$(H^+)_m$	Measured (H^+) determined from measured pH
$\triangle$	The difference between the pH of any point on the pH vs absorbance curve and the pH at the curve's maximum

1. Introduction

General introduction

Palladium is a transition element and is located vertically in the periodic table between Pt and Ni. Like platinum this element forms square complexes in the +2 valence state. The current theory is that square complexes are tetragonally distorted octrahedral structures of the type:



where the S ligands may be solvent molecules or any other species present and are loosely held at the apices.

In a solution of $Pd(NH_3)_2Cl_2$, a well-known square complex of Pd(II), we would expect to find the following species present in equilibrium: $^*Pd(NH_2)_2Cl_2$, $Pd(NH_3)_3Cl^+$, $Pd(NH_3)_4^{++}$, $^*Pd(NH_3)_2Cl(H_2O)^+$, $Pd(NH_3)_3H_2O^{++}$, and $^*Pd(NH_3)_2(H_2O)_2^{++}$, where * prefix indicates that cis and trans isomers probably exist. Reinhardt[1] showed in a study of the solubility of $Pd(NH_3)Cl_2$ that aquation is greatly repressed by the presence of chloride ion. For this reason, equilibrium studies will generally only be made on solutions of high (Cl^-) so that the aquated species may be ignored.

When HCl is added to a solution of $Pd(NH_3)_4^{++}$, a substitution reaction occurs and $Pd(NH_3)_2Cl_2$ is formed. The reverse substitution

[1]Reinhardt, R. A., Inorg. Chem., 1, 839 (1962)

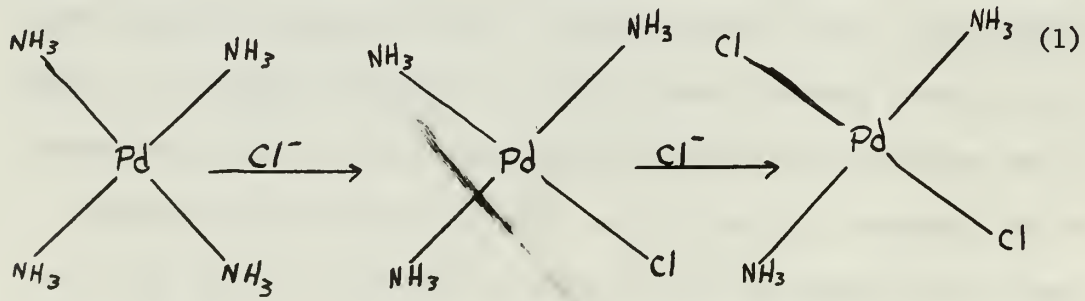
may be caused by adding NH_3 to a solution of $Pd(NH_3)_2Cl_2$; however, this latter reaction appears to proceed much more rapidly than does the former. The study of these substitution reactions will be the main object of this thesis.

The trans effect and cis-trans isomerism

The concept of a "trans effect" in the replacement reactions of square complexes was first introduced by Chernyaev[2] when he called attention to the fact that a negative ligand such as Cl^- has a greater labilizing effect on a group trans to it than it does on groups in cis positions. The order of ligands as related to this phenomenon is

$$H_2O < OH^- < NH_3 < Cl^- < Br^- < I^- \frown NO_2^- \frown PR_3 << CO \frown C_2H_4 \frown CN^-.$$

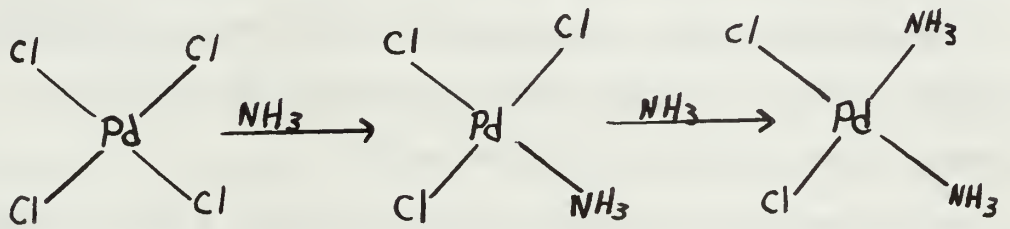
The trans effect has proved very useful in synthesis procedures. For the palladium system under study, the addition of HCl to tetramminepalladium (II) results in trans-dichlorodiamminepalladium (II) as shown in (1)



(1)

[2] Chernyaev, I. I., Ann. Inst. Platine U.S.S.R., 4, 261 (1926).

while the addition of ammonia to tetrachloropalladate (II) under certain conditions may be used to synthesize the cis isomer[3] as shown in (2).



(2)

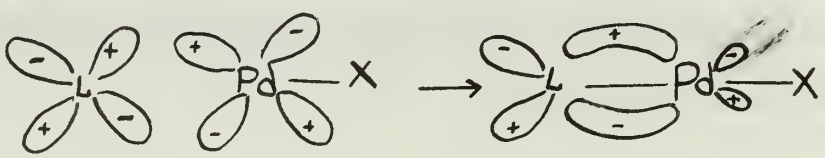
In both of these reactions we apparently observe the superior trans directing influence of Cl^- relative to NH_3. Stereospecificity of final product, however, does not necessarily arise from a trans effect. For instance, in (1) if both cis and trans isomers were formed with possible equilibrium between the two species, only the trans isomer would be observed to precipitate from solution because of its lesser solubility. Likewise, in (2) if the $PdCl_4^=$ does not show a trans effect with the addition of NH_3 and actually forms both cis-and trans-$Pd(NH_3)_2Cl_2$, we could explain the isolation of the cis isomer on the basis of trans-isomer reacting very rapidly with NH_3 to form the more soluble $Pd(NH_3)_3Cl^+$ and $Pd(NH_3)_4^{++}$ species while the possibly less reactive, but highly insoluble, cis-isomer precipitates from solution. In other words, it may not be justifiable to predict the existence of a trans effect for a particular substitution reaction on the basis of final product alone.

[3]Grinberg, A. A. and V. M. Shulman, Dokl. Akad. Nauk SSSR, 215 (1933).

Basolo and Pearson[4] define trans effect as the effect of a coordinated group upon the rate of substitution reactions of ligands opposite to it. Accordingly, metals in which the rate influence of opposite, or trans groups, is definitely greater than the influence of adjacent, or cis groups, are considered to show a trans effect. It is this definition which will be used in this thesis to determine the extent to which the trans effect is operative for the chloro and ammine square complexes of palladium (II).

Two different but not mutually exclusive theories which attempt to explain the trans effect may be found in current literature.[4,5] One, the bond weakening theory attempts to justify the observed effect in terms of the tendency of the various ligands to weaken, by electrostatic and polarization effects, the bonds to ligands trans to themselves. This theory cannot explain fully the order of ligands in the trans effect but can explain both SN1 and SN2 mechanisms since in either case the least strongly bonded ligand would be expected to be the leaving group.

Second, the "π -bonding theory" which attempts to describe the trans effect as a function of the ligands' ability to form d$_{\pi}$-π bonds with the metal atom. This theory can thus only be applied to ligands such as Cl^- which have vacant d-orbitals.



(3)

[4]Basolo, F. and R. G. Pearson in Progress in Inorganic Chemistry, Vol. 4, edited by F. A. Cotton, Interscience Publishers, New York, 1962, pp. 381-428

[5]Cotton, F. A. and G. Wilkinson, Advanced Inorganic Chemistry, Interscience Publishers, 1962, pp. 552-554.

This theory is illustrated schematically above and we observe that the presence of a strongly electron accepting orbital on ligand L withdraws electron density in the $d\pi$ orbital which it has in common with ligand X trans to it. The region near ligand X becomes more accessible to attack by a nucleophilic group. Hence, this theory can only effectively explain SN2 mechanisms and only extends to ligands with vacant d-orbitals. Ligands such as H_2O and NH_3 which cannot π-bond in this manner must be treated by the bond weakening theory.

Some studies have been made of the relative stabilities of cis and trans isomers of Pt (II) complexes and also of the equilibrium which exists between the two isomeric species. Chernyaev et al[6], made measurements of the heats of reaction of some chloroammine platinum (II) complexes with ammonia to give tetrammine platinum (II). Their results have been analysed by Basolo and Pearson[4] who conclude that trans-$Pt(NH_3)_2Cl_2$ is more stable than the corresponding cis isomer.

Chatt and Wilkins[7] studied the cis-trans isomeric equilibrium of PtA_2X_2 compounds where A = phosphines, arsines, and stibines and X = halide ions. Their studies were made on benzene solutions and the relative amounts of the isomers were determined by dielectric constant measurement. In all cases they observed much less cis than trans isomer present at equilibrium. It is interesting to note that their data show that the trans isomer owes its greater stability to

[6]Chernyaev, I. I., V. A. Palkin, R. A. Baranova, and N. N. Kuz'mina, J. Inorg. Chem. (U.S.S.R.), 5, 693 (1960).

[7]Chatt, J., and R. G. Wilkins, J. Chem. Soc., 1956, p. 525.

the large entropy term which accompanies cis-to-trans conversion. The cis isomer is more highly solvated due to its large dipole and some solvent molecules will be released upon conversion to the trans form. A similar study which they made of $Pd(Sb(C_2H_5)_3)_2Cl_2$ shows that the trans isomer is likewise greatly favored.

Equilibrium quotient determination

Knowledge of the equilibrium quotients involved in the substitution reactions under study was considered essential to a better understanding of stoichiometry and kinetics. Furthermore, the extinction coefficients of intermediate species could be evaluated only if the equilibrium quotients were known.

For the reactions

$$Pd(NH_3)_4^{++} + H^+ + Cl^- \rightleftharpoons Pd(NH_3)_3Cl^+ + NH_4^+ \quad (4)$$

$$Pd(NH_3)_3Cl^+ + H^+ + Cl^- \rightleftharpoons Pd(NH_3)_2Cl_2 + NH_4^+ \quad (5)$$

The equilibrium quotients for the two equilibria may be expressed respectively as (6) and (7)

$$\frac{(Pd3)(NH_4^+)}{(Pd4)(H^+)(Cl^-)} = K_1' \quad (6)$$

$$\frac{(Pd2)(NH_4^+)}{(Pd3)(H^+)(Cl^-)} = K_2' \quad (7)$$

The abbreviated symbols used in writing (6) and (7) are defined in the Table of Symbols and brackets about species imply molar concentrations. K_1' and K_2' may be further defined in terms of the thermodynamically-defined equilibrium constants and the activity coefficients of the various species. However, as is usual in studies of this type, it will be assumed that the activity coefficients and hence the equilibrium quotients remain constant in a solution of high, constant ionic strength.

By utilizing the expression for the acidity quotient, K_a, of the ammonium ion, we may write (6) and (7) in the form

$$\frac{(Pd3)(NH_3)}{(Pd4)(Cl^-)} = K_1'' \quad ; \quad K_1'' = K_1' K_a \tag{8}$$

$$\frac{(Pd2)(NH_3)}{(Pd3)(Cl^-)} = K_2'' \quad ; \quad K_2'' = K_2' K_a \tag{9}$$

Equations (8) and (9) express the equilibrium relationships which exist between the chloride and ammonia ligands and the various complex species. That is,

$$Pd(NH_3)_4^{++} + Cl^- \rightleftharpoons Pd(NH_3)_3Cl^+ + NH_3 \tag{10}$$

$$Pd(NH_3)_3Cl^+ + Cl^- \rightleftharpoons Pd(NH_3)_2Cl_2 + NH_3 \tag{11}$$

It is the values of K_1'' and K_2'' which we are interested in determining.

If the ammonium and chloride ion concentrations in solution are made large, they may be considered constant throughout the reactions and expressions (6) and (7) may be written

$$\frac{(Pd3)}{(Pd4)(H^+)} = K_1 \quad ; \quad K_1 = \frac{K_1'(Cl^-)}{(NH_4^+)} \tag{12}$$

$$\frac{(Pd2)}{(Pd3)(H^+)} = K_2 \quad ; \quad K_2 = \frac{K_2'(Cl^-)}{(NH_4^+)} \tag{13}$$

Using (12) and (13) we may express the complex concentrations as

$$(Pd3) = K_1(Pd4)(H^+) \tag{14}$$

$$(Pd2) = K_2(Pd3)(H^+) = K_1K_2(Pd4)(H^+)^2$$

The spectrophotometrically measured absorbance of a solution containing these complex species can be expressed

$$A = L(a_4(Pd4) + a_3(Pd3) + a_2(Pd2)) \tag{16}$$

Where A = absorbance; a_2, a_3 and a_4 are the molar extinction coefficients for their respective complex species; and L = light path

length (cell thickness). It is assumed here that all other species present in solution are transparent at the wavelength used.

Substitution of (14) and (15) into (16) gives (17):

$$A = L \left\{ (Pd4) \left[a_4 + K_1(H^+)a_3 + K_1K_2(H^+)^2 a_2 \right] \right\} \qquad (17)$$

If we now define the total palladium concentration by the symbol B, so that in terms of the individual concentrations

$$B = (Pd2) + (Pd3) + (Pd4) = (Pd4) \left[1 + (H^+)K_1 + (H^+)^2K_1K_2 \right] \qquad (18)$$

Division of (17) by (18) results in a function (19) which, when L and B remain constant, has only the absorbance, A, and the hydrogen ion concentration, (H^+), as its variables.

$$A = BL \left[\frac{a_4 + K_1(H^+)a_3 + K_1K_2(H^+)^2 a_2}{1 + K_1(H^+) + K_1K_2(H^+)^2} \right] \qquad (19)$$

Now is a wave length is selected for which a_3 is larger than a_2 and a_4, a plot of absorbance versus PH values will result in a curve such as that of Figure 1. This curve can be treated mathematically by a method similar to that of Thamer and Voigt[8] to give values for K_1 and K_2 from equations (20) and (21) - the derivations of which are presented in Appendix I.

$$K_1K_2 = \frac{A_m - A_4}{(H_m^+)^2 (A_m - A_2)} \qquad (20)$$

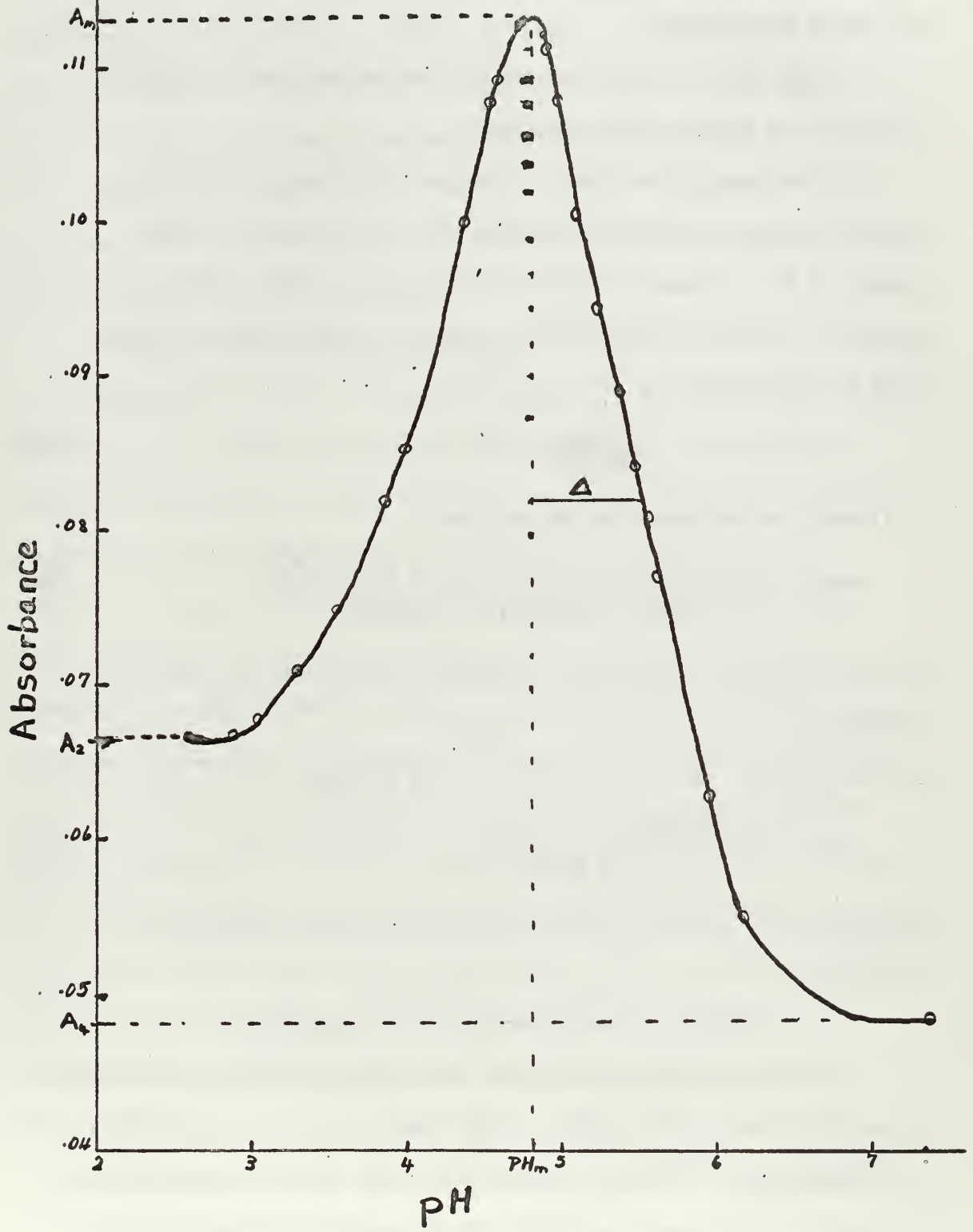
$$K_1 = \frac{(A_m-A_4)(A-A_2)10^{-\Delta} - 2(A_m-A_4)(A_m-A_2) + (A-A_4)(A_m-A_2)10^{\Delta}}{(H_m^+)(A_m-A_2)(A_m-A)} \qquad (21)$$

As indicated in Figure 1, A_m and (H_m^+) are located at the maximum on the curve, A_4 is the minimum absorbance at high PH values and is assumed to be due entirely to Pd4, A_2 is the minimum absorbance at

[8] Thamer, B.J., and A. F. Voigt: J. Phys. Chem., 56, 225 (1952)

Figure 1

plot of absorbance vs pH, Temp = 25°C, λ = 330 mμ



low pH values and is assumed to be due entirely to Pd2. Any point on the curve yields a set of values for A and Δ , where A is the absorbance and Δ is the difference between the pH at the point and the pH at the maximum.

Values of K_1 and K_2 obtained by this method can be further refined by a least square treatment.

In this particular study, equations (20) and (21) will be applied to a system which is assumed to contain only the trans isomer of Pd2. Should conditions be such that both isomers are present in equilibrium, then, an additional equilibrium quotient must be considered

$$\frac{(c\text{-}Pd2)}{(Pd3)(H)} = K_3 \tag{22}$$

(19) must now be rewritten in the form

$$A=BL\ \frac{a_4 + K_1(H)a_3 + K_1K_2(H)^2a_2 + K_1K_3(H)^2a_2^*}{1 + K_1(H) + K_1K_2(H)^2 + K_1K_3(H)^2} \tag{23}$$

with a_2^* defined as the molar extinction coefficient for the cis-$Pd(NH_3)_2Cl_2$.

For the special case of $a_2 = a_2^*$, (23) becomes

$$A=BL\ \frac{a_4 + K_1(H)a_3 + K_1K(H)^2a_2}{1 + K_1(H) + K_1K(H)^2} \quad ; \quad K = K_2 + K_3 \tag{24}$$

Equations (20) and (21) still apply to (24) but do not apply to (23).

Kinetics and mechanism of substitution

It was mentioned earlier that the addition of excess HCl to a solution of $Pd(NH_3)_4^{++}$ results in the formation, initially at least, of $Pd(NH_3)_2Cl_2$. It will be shown later that only the trans species is likely to be formed initially. Furthermore, the rate of this

substitution reaction is slow enough to be measured by conventional instrumental methods - with potentiometry and UV-spectrophotometry the favored modes. The reverse reactions which obtain, however, when ammonia is added to a $Pd(NH_3)_2Cl_2$ solution are very fast even at low temperatures and special mixing and measuring techniques would be required if the rates were to be measured directly.

Experimental observations, the exact nature of which will be discussed under the experimental part of this thesis, show that the reaction rates for the reactions

$$Pd(NH_3)_4^{++} + H^+ + Cl^- \rightleftharpoons Pd(NH_3)_3Cl^+ + NH_4^+ \qquad (25)$$

$$Pd(NH_3)_3Cl^+ + H^+ + Cl^- \rightleftharpoons Pd(NH_3)_2Cl_2 + NH_4^+ \qquad (26)$$

are independent of the hydrogen ion concentration but dependent on the concentrations of complex and chloride ion. Although a simple first-order relationship for the chloride ion does not appear to obtain, it seems safe to assume that, for chloride concentrations large enough to be considered constant throughout the reaction, pseudo first-order kinetics for the step-wise forward reactions will be observed when conditions are such that the reverse reactions can be ignored. It appears that the only function of the hydrogen ions is to neutralize the NH_3 leaving group, thus allowing the forward reactions to proceed. Therefore, a highly acidic medium will provide conditions where, for at least a good part of the total reaction time, only the kinetics of the forward reactions will be observed. It should be mentioned here that it is the extreme inertness of the trans-$Pd(NH_3)_2Cl_2$ to further substitution which makes it possible to add excess acid in the manner mentioned and then limit attention to only the two replacements, (25) and (26).

For those conditions which have been described, that is, constant chloride concentration and excess acid, the observed kinetics should be the kinetics of two first order reactions in series of the type

$$A \xrightarrow{k_1} B$$

$$B \xrightarrow{k_2} C$$

where for our particular system A = Pd4, B = Pd3, C = Pd2, and k_1 and k_2 are the pseudo first-order rate constants for a given temperature and (Cl^-).

Now, using A, B, and C also to represent molar concentrations of the corresponding species, the rate laws may be written

$$\frac{dA}{dt} = -k_1 A \tag{27}$$

$$\frac{dB}{dt} = k_1 A - k_2 B \tag{28}$$

$$\frac{dC}{dt} = k_2 B \tag{29}$$

The integration of these differential equations, as presented in Appendix II, yields the corresponding integrated rate equations:

$$A = A_o e^{-k_1 t} \tag{30}$$

$$B = \frac{A_o k_1 (e^{-k_1 t} - e^{-k_2 t})}{k_2 - k_1} \tag{31}$$

$$C = A_o \left[1 + \frac{1}{k_1 - k_2} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right] \tag{32}$$

A_o is the initial concentration of species A. It is assumed that $B_o = C_o = 0$.

Frost and Pearson[9] suggest writing equations (30), (31), and (32) as a simpler form by introducing dimensionless parameters and variables. Using their notation we let

$$\alpha = \frac{A}{A_o}, \quad \beta = \frac{B}{A_o}, \quad \gamma = \frac{C}{A_o}, \quad \tau = k_1 t, \quad K = \frac{k_2}{k_1}.$$

Then the equations become:

$$\alpha = e^{-\tau} \tag{33}$$

$$\beta = \frac{1}{K-1}\left(e^{-\tau} - e^{-k\tau}\right) \tag{34}$$

$$\gamma = 1 + \frac{1}{1-K}\left(Ke^{-\tau} - e^{-K\tau}\right) \tag{35}$$

An additional variable δ is introduced and defined as $\delta = \beta + 2\gamma$. Therefore

$$\delta = 2 - \frac{(1-2K)}{(1-K)} e^{-\tau} - \frac{1}{(1-K)} e^{-K\tau} \tag{36}$$

It is important to observe that since $\delta = \frac{B}{A_o} + 2\frac{C}{A_o}$, then, $1/2\,\delta = \frac{1/2B + C}{A_o}$ = fraction of reaction completed. Therefore, $50\,\delta$ = percent of reaction completed. Equation (36) makes it possible to calculate τ-values for various values of K and δ such as those in Table 8. For our kinetics study, $50\,\delta$ will be related to the amount of H^+ that is consumed during the reaction (see equation (40)).

A graphical method of solution has been suggested.[10] Using the values calculated from equation (36), plots of $50\,\delta$ versus $\ln \tau$ are made so as to construct a family of curves with each member

[9]Frost, A. A. and R. G. Pearson, Kinetics and Mechanism, 2nd edition, John Wiley and Sons Inc., New York, 1961, pp. 166-171

[10]French, D., J. Am. Chem. Soc., 72, 4806 (1960)

identified by a particular value of K. Now, since $\tau = k_1 t$ and $\ln \tau = \ln k_1 + \ln t$, a plot of experimentally determined values of percent reaction versus the logarithm of the time will be the same as one of the family of curves - that one having the same K- but shifted horizontally by an amount equal to $-\ln k_1$. Hence, curve matching will determine the value of K while either the shift of ln t or the ratios $\frac{\tau}{t}$ for corresponding values of percent reaction and $50\,\delta$ will determine the value of k_1.

A time ratio method of solution has been used by Swain[11] and is presented in modified form by Frost and Pearson[9]. This method is very similar to the graphical method just described but simplifies the determination of the value of K. They let τ_1 and τ_2 be the values of τ corresponding to the values δ_1 and δ_2. The ratio τ_2/τ_1 is equal to the ratio t_2/t_1 of the experimental times whose percent reaction corresponds to the $50\,\delta$ of the τ-values. However, since τ_2/τ_1 and hence t_2/t_1 values are functions only of K, a table of K versus τ_2/τ_1 values such as those of Table 9 will lead to a value of K. The τ/t quotients will then yield the value of k_1.

Most kinetic studies of square complexes to date have been made on aqueous solutions of platinum (II) complexes. Earlier such kinetic studies[12] suggested that the substitution reactions studied fell into two categories: (1) those that were first order in complex but zero order in reactant; (2) those that were first order in both the

[11]Swain, C. G., J. Am. Chem. Soc., 66, 1696 (1944)

[12]Banerjea, D., F. Basolo, and R. G. Pearson, J. Am. Chem. Soc., 82, 4055 (1957)

complex and the reactant and faster than those of the first category. In general, the reactants of category (1) are low in the trans-effect series while those of category (2) are high in the series.

More detailed studies now indicate that there is always a reaction involving the solvent as a nucleophilic reagent, for example, Basolo et al[13] found the reaction

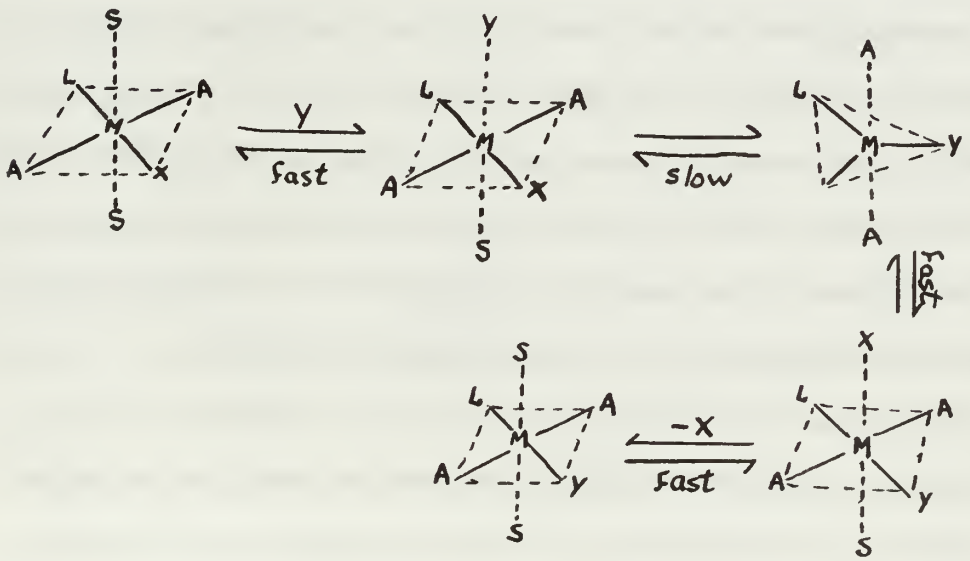
$$Pt(dien)Cl^{+} + Y^{-n} = Pt(dien)Y^{+2-n} + Cl^{-}$$

to obey the rate law

$$Rate = K_1(Pt(dien)Cl^{+}) + k_2(Pt(dien)Cl^{+})(Y)$$

where k_1 is a first-order rate constant for the solvent controlled reaction and k_2 is a second-order rate constant for reaction with Y.

A bimolecular displacement mechanism through a trigonal bipyramid transition state has been proposed by Basolo and Pearson[4] for the substitution reactions of square complexes:



[13]Basolo, F., H. B. Gray, and R. G. Pearson, J. Am. Chem. Soc., 82, 4200 (1960)

They also suggest the possibility of a bimolecular displacement mechanism through a square pyramid intermediate. Although evidence may be cited for each of these possible transition states, it appears that the trigonal bipyramid structure is the favored of the two.

Banerjea and Tripathi[14] have made kinetic studies of some substitution reactions of palladium (II) complexes. They found that $Pd(en)Cl_2$ reacts faster by several powers of ten than trans-$Pd(NH_3)_2(NO_2)_2$. Since this is contrary to the trans effect order of $NO_2^- > Cl^- > NH_3$ or en for Pt(II) they concluded that the trans effect is not operative in Pd(II) complexes. They also reported that the substitutions in Pd(II) are of the SN2 type. Reinhardt[1] has noted, however, that conductivity measurements of Palladium complexes in aqueous solution may be rendered unreliable by decomposition of the complex such as occurs for $Pd(NH_3)_2Cl_2$ and $Pd(Cl)_4^=$. Basolo and Pearson[4] likewise note that the reported results are questionable in view of the observation that reactions of Pd(II) complexes are generally very much faster than some of the rates reported in the study. It would appear to the author of this thesis that it is a gross error to use a limited study of one complex of Pd(II) to arrive at the conclusion apriori that the trans effect is necessarily inoperative for all complexes of Pd(II).

Jonassen and Cull[15] studied the directive influence of the nitro group in complexes of Pd(II) and propose substitution mechanisms which can be explained only if trans elimination is assumed.

[14]Banerjea, D., and K. K. Tripathi, J. Inorg. Nuclear Chem., 7, 78 (1958)

[15]Jonassen, H. B., and N. L. Cull, J. Am. Chem. Soc., 73, 274 (1951)

2. Apparatus and materials

pH measurements were made with a Beckman model Research pH Meter with a general purpose external shielded glass electrode and a frit junction calomel internal reference electrode. Readability of this meter is .0005 pH and repeatability if $\pm$.0005 pH units.

Standard commercial buffers used to standardize the pH meter were:

pHydrion pH 3.00 $\pm$ .05 @ 25.0°C

pHydrion pH 5.00 $\pm$ .05 @ 25.0°C

All absorbance measurements used quantitatively in the equilibrium and kinetic studies were made on a Beckman model DU Spectrophotometer equipped with a thermostated cell compartment.

Beckman model DB and model DK1A spectrophotometers equipped with recorders were used for scanning over various ranges of wavelength. Cells were not thermostated in these instruments and percent transmittance measurements were used only to make qualitative observations.

A matched pair of Beckman quartz 1 cm cells was used in all measurements. Calibration checks showed that these cells were well matched to within the reading accuracy of the instruments. Aqueous solutions of the same salt as contained in the sample were used as references.

Temperature control for all instrumental work was effected through a constant temperature bath using an electronic control relay and microset thermostat system capable of holding the temperature constant to $\pm$ .02°C. Water from the bath was circulated by a small pump through the jackets of the thermostated DU cell compartment.

All standard solutions were prepared using freshly boiled distilled water. Concentrations of the various solutes were determined as follows:

Ammonium chloride by careful weighing of reagent grade NH_4Cl which had dried for several days in a desiccator. Similarly, sodium chloride was determined by careful weighing of reagent grade NaCl which had been oven dried.

Palladium was determined by a gravimetric procedure involving precipitation of the palladium as the insoluble salt of dimethylglyoxime. The procedure followed was substantially that of Treadwell and Hall[16] and good precision was observed.

Hydrochloric acid concentrations were determined using prescribed analytical procedures.[17] Potassium biphthalate (certified as primary standard) was used as the primary standard to standardize a NaOH solution prepared from low-carbonate 50% NaOH solution. The HCl solution was then titrated against the standard NaOH solution to phenolphthalein end-point. Dilute solutions of HCl were prepared by diluting pipetted volumes of the standardized HCl solution in a volumetric flask.

Ammonia solutions were prepared fresh when concentrations were to be used quantitatively and were titrated against the standard HCl solution. Methyl red and methyl orange indicators were both

[16]Treadwell, F. P. and W. T. Hall, Analytical Chemistry, Vol II, John Wiley and Sons, Inc., New York, 1942, p. 140

[17]Pierce, W. C., D. T. Sawyer, and E. L. Haenisch, Quantitative Analysis, 4th edition, John Wiley and Sons, Inc., New York, 1963, pp. 248-249

used and gave consistent results. Dilute solutions of NH_3 were prepared by diluting a known volume of the standardized solution in a volumetric flask.

Solid $Pd(NH_3)_4Cl_2.H_2O$ was prepared through the following reaction procedures: Palladium chloride was dissolved in concentrated HCl solution and treated with NH_3 to form the insoluble, pink-colored complex $Pd(NH_3)_4PdCl_4$. The precipitate was collected, washed thoroughly and then dissolved in concentrated ammonia. The solution was filtered and then evaporated at room temperature to yield the pale-yellow crystals of $Pd(NH_3)_4Cl_2.H_2O$.

3. Determination of the hydrogen ion concentration.

The glass and reference electrodes used with most pH meters are generally standardized against a buffer solution of known pH, or, if precise results are required, a hydrogen electrode may be used as a standard. The meter can then be used to measure the hydrogen ion activity in other dilute solutions. However, the research of this thesis demands a knowledge of the hydrogen ion concentration in a solution of high, constant ionic strength. Reinhardt[18] suggested a technique which allows for the conversion of (H^+) values obtained from pH meter measurements to actual concentrations.

According to this technique small increments of C molar HCl solution are delivered with careful measurement to a known volume, V_o, of NH_4Cl solution of the same concentration as the system we wish to study. The pH is measured after each addition of acid. Since the contribution of hydrogen ion from the dissociation of

[18]Reinhardt, R. A., in private communication, 1966

NH_4^+ and water will be small except for the addition of only a very small amount of acid, we can consider that the (H^+) is a function only of the added acid. Therefore, if V is the volume of acid that has been added,

$$(H^+) = D(H^+)_m = \frac{(V)(C)}{V+V_o}$$

$$(H^+)_m(V+V_o) = \frac{(V)(C)}{D} \qquad (37)$$

where $(H^+)_m$ is the value of hydrogen ion measured on the pH meter and D is a conversion factor.

Equation (37) indicates that a plot of the product of $(H^+)_m$ and the total volume versus the volume of acid solution added will yield a value for the conversion factor.

4. The acidity quotient of ammonium ion.

The value of K_a, the acidity or hydrolysis constant of ammonium ion, is a well-established thermodynamic value; however, for our study we require the value of the acidity quotient of the ion in a solution of high ionic strength. The expression for the acidity quotient which will also be designated as K_a may be written as

$$K_a = \frac{(NH_3)(H^+)}{(NH_4^+)} \qquad (38)$$

The value of K_a is a function of ionic strength and therefore must be experimentally determined for the particular solution which is under study. Bjerrum[19] outlined a method of determining a value of K_a and it is essentially according to his method that a value was determined for a 1.0 molar NH_4Cl solution as follows.

[19]Bjerrum, J., Metal Ammine Formation in Aqueous Solution, P. Haase and Son, Copenhagen, 1941

Small, carefully measured, volume increments of dilute C molar NH_3 solution were added to an M molar solution of NH_4Cl and the pH measured after each addition. Since the degree of dissociation of ammonium ($NH_4^+ = NH_3 + H^+$) is small, we can assume as an approximation that all of the NH_3 in solution arises from the added ammonia. Therefore, if V_o was the original volume of the NH_4Cl solution and V is the volume of NH_3 solution that has been added,

$$(NH)_3 = \frac{(V)(C)}{V_o + V} \quad \text{and} \quad (NH_4^+) = \frac{(V_o)(M)}{V_o + V}$$

Substitution of these values into equation (38) gives

$$(H^+) = K_a \frac{(NH_4^+)}{(NH_3)} = K_a \frac{(V_o)(M)}{(V)(C)}$$

or in terms of the measured value of (H^+),

$$(H^+)_m = K_a \frac{(V_o)(M)}{(D)(V)(C)} \tag{39}$$

where D must be determined from equation (37). We see from equation (39) that a plot of (H^+) versus 1/V will enable us to calculate a value for K_a.

Data for the determination of the conversion factor D, are contained in Table 1 and the plot for the first run is given in Figure 2. The slopes of the straight line plots for runs 1 and 2 were 9.75×10^{-3} and 9.74×10^{-3} respectively, and in accordance with equation (37) the average value of the conversion factor for this particular determination was 1.091.

Data for the determination of the value K_a for ammonium ion in 1.0 molar NH_4Cl solution at 25°C are presented in Table 2. A plot of the first run of this data is given in Figure 3. The slopes of

Figure 2.

Plot of data of Table 1 for the determination of the (H^+) conversion factor.

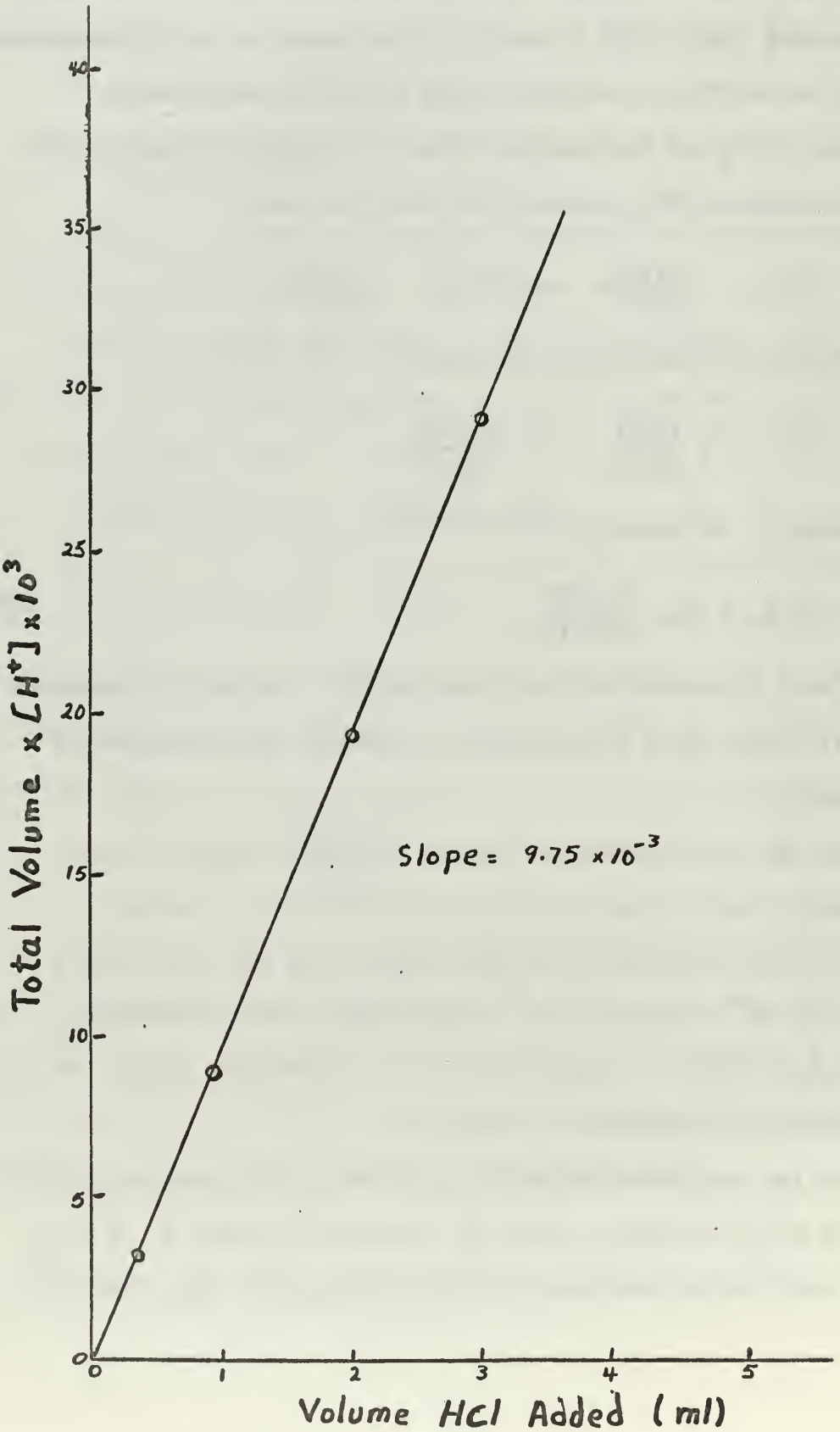
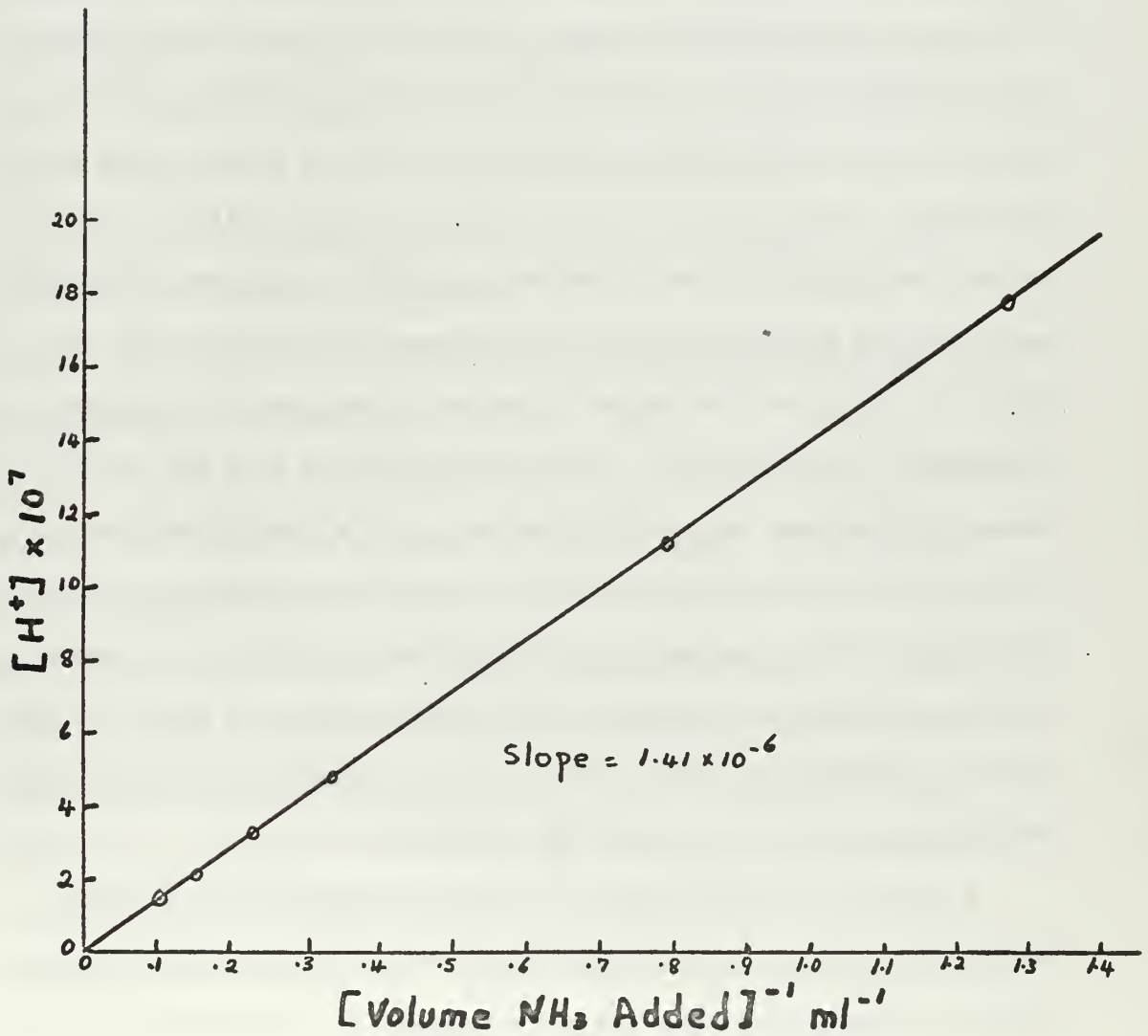


Figure 3

Plot of the data of Table 2 for the determination of the equilibrium quotient for NH_4^+ at 25°C.



the straight line plots for runs 1 and 2 were 1.41×10^{-6} and 1.43×10^{-6} for an average value of 1.42×10^{-6}. Using this value together with the value calculated for D gives a value for K_a of 4.77×10^{-10}.

5. Experimental measurements.

Equilibrium quotient data

In the introductory part of this topic we outlined the method that would be used to determine the desired equilibrium quotients. Before outlining the experimental procedures that were used to obtain the necessary data, a word should be said about the limitations of this method as applied to the system under study. First, we require a solution of high ionic strength, and the salt used to provide the ionic strength must not coordinate with Pd(II) (chloride excepted), must not react unfavorably with any other species present, and must not absorb at 330 $m\mu$, the wavelength to be used. Nitrates absorb at this wavelength and may coordinate with Pd. Ammonium perchlorate was tried but proved unsatisfactory because the precipitation of $KClO_4$ at the tip of the calomel electrode caused erratic pH meter performance. Additionally, it must be remembered that NH_4^+ and Cl^- concentrations must be fairly large so as to be considered constant. A high chloride concentration further ensures the repression of acid hydrolysis of the complex. For the reasons discussed, a 1.0 molar solution of NH_4Cl was selected as the ionic medium. A bonus for our choice is noted: the (NH_4^+) and (Cl^-) are essentially equal and will therefore cancel in equations (12) and (13).

A second limitation exists in the concentration of palladium which can be used. Trans-$Pd(NH_3)_2Cl_2$, being both non-ionic and non-polar, is the least soluble of the complexes in our series. For this

reason the total Pd concentration must not exceed the solubility of this least soluble species. Concentrations of about .0008 molar were found to be just within this solubility limit at 25°C.

A third area where caution must be observed is that of equilibration time. $Pd(NH_3)_2Cl_2$ in a solution of high (H^+)will eventually be converted to $Pd(Cl)_4^=$. Fortunately, this further substitution proceeds very slowly but the danger of charge transfer absorption from $Pd(Cl)_4^=$ dictates that unnecessary time delay be avoided. The possible conversion of trans to cis isomer requires that all of the complex should initially be in the form of $Pd(NH_3)_4^{++}$ or $Pd(NH_3)_3Cl^+$, that is, at a high pH, and again unnecessary delay should be avoided. This topic is the subject of further discussion in this thesis.

With the above-mentioned limitations in mind, the following experimental procedure was observed.

(1) A stock solution of $Pd(NH_3)_4^{++}$ in 1.0 molar NH_4Cl was prepared and analysed for palladium.

(2) 50 ml aliquots of the stock solution were pipetted into 150 ml beakers which were then allowed to come to thermal equilibrium in the water bath at 25°C.

(3) The pH of the solutions was varied by adding small increments of either .1 or 1.0 molar HCl with a fine dropper. The high pH values were attained by the addition of NH_3. The maximum volume added did not exceed .10 ml for any one solution. Each solution was used for just one pH-absorbance determination.

(4) Each solution was allowed to equilibrate 30-40 minutes prior to making measurements. Since the reaction in 1.0 molar Cl^- is

essentially complete within 8 minutes, this equilibration was considered adequate.

(5) pH and absorbance measurements were made and recorded. Both the pH meter and the DU spectrophotometer were allowed at least a one hour warmup period prior to taking the first measurement. In addition, of course, the pH meter was calibrated and standardized prior to use. 1.0 molar NH_4Cl solution was used in the reference cell for absorbance measurements.

Sets of data for three different stock solutions are presented in Table 3. A plot of the data from Table 3a is given in Figure 1.

Kinetics data

Two methods of observing the rate of the substitution reactions were employed. In both methods the observations were made on a solution of $Pd(NH_3)_4^{++}$ of known chloride concentration to which excess HCl was added. The first method then consisted of measuring pH against time while the second involved measuring absorbance versus time at definite wave lengths. In the former method we are somewhat restricted in the amount of HCl which can be added. If the pH is made too small there will not be enough change to give good readings. Fortunately, the high sensitivity of the Research pH Meter still allows us to start at pH values of about 2. It is desirable of course to keep the pH as low as possible so as to eliminate a maximum of the reverse kinetics. The following procedure was observed for taking pH versus time measurements:

(1) $Pd(NH_3)_4^{++}$ solutions with added NaCl to give the desired (Cl^-) were prepared. A small amount of ammonia was added to each to ensure that all Pd was in the form of $Pd(NH_3)_4^{++}$.

(2) The complex solutions, together with standardized HCl solutions, were maintained at constant temperature in the water bath.

(3) 50 ml aliquots of complex solution were pipetted into 150 ml beakers which were secured in the bath. The electrodes were then inserted into the solution and allowed to come to thermal equilibrium.

(4) A 5.0 ml aliquot of the HCl was added to the complex with rapid stirring. The electric timer was started when approximately half of the acid solution had been added.

(5) pH values were read - usually every 20 sec - until the reaction appeared to be essentially complete as observed by meter readings.

Data of measured time versus (H^+) for complex solutions of various chloride concentrations at 25°C are presented in Table 4. Plots of some of these data are given in Figure 4 to illustrate the effect of (Cl^-) on reaction rate.

Measured (H^+) versus time data for a solution 1.0 molar in NH_4Cl at various temperatures are presented in Table 5 and plotted in Figure 5 to illustrate the effect of temperature on reaction rate.

The only variation of the above-described technique required for taking absorbance versus time measurements is that the stirred, acidified complex solution is quickly transferred to the sample cell in the thermostated cell compartment of the spectrophotometer so that absorbance may be observed and recorded.

Measured absorbance versus time data for a complex solution 1.0 molar in NH_4Cl at 25°C and at wavelengths of 300 and 385 mμ are given in Table 6. A plot of this data is given in Figure 6. It should also be mentioned that more concentrated HCl solution was used since low pH does not present a reading problem as it does for pH measurement.

Figure 4

Plot of (H^+) versus time for various (Cl^-) at 25°C

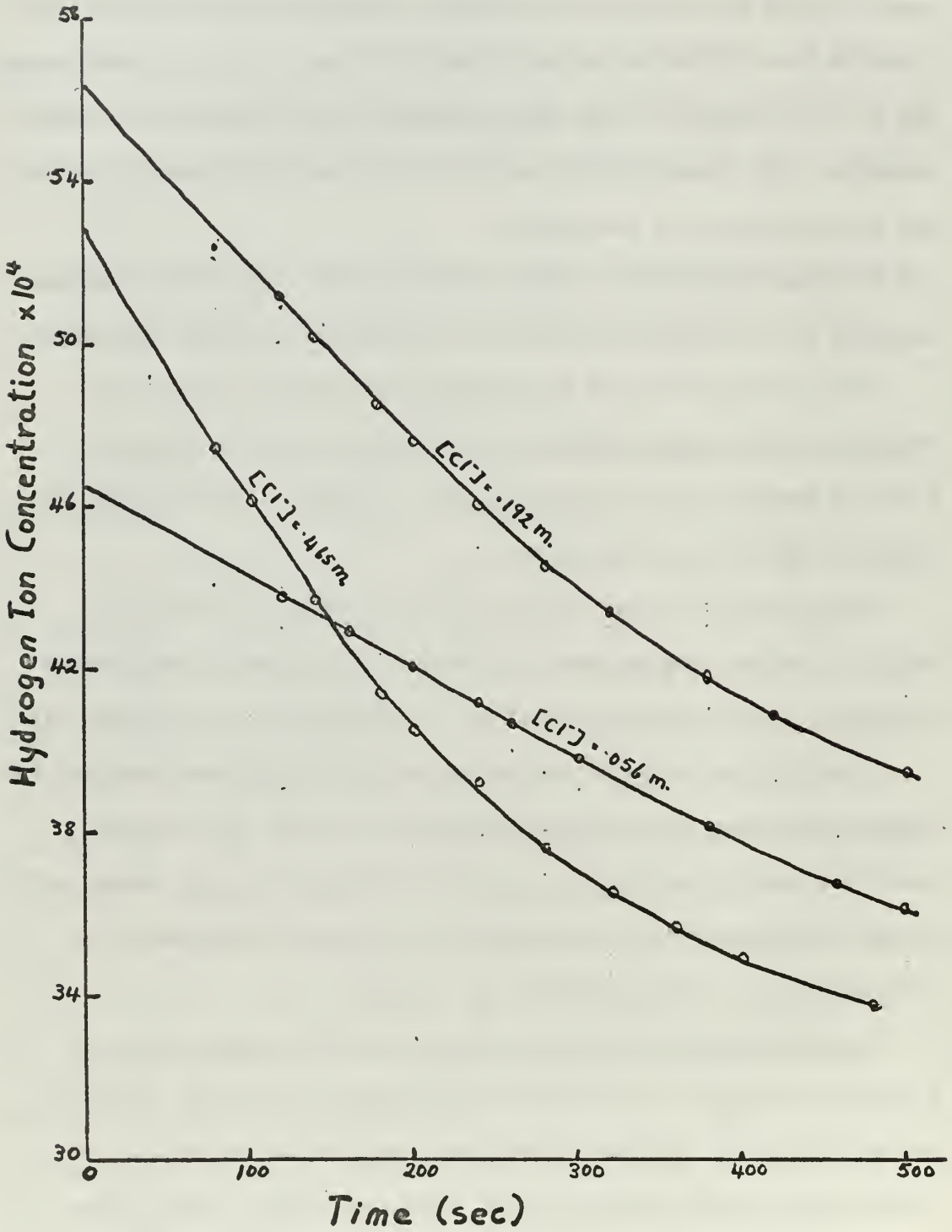


Figure 5

Plot of (H^+) versus time to show the effect of temperature. (Cl^-) = 1.0 molar.

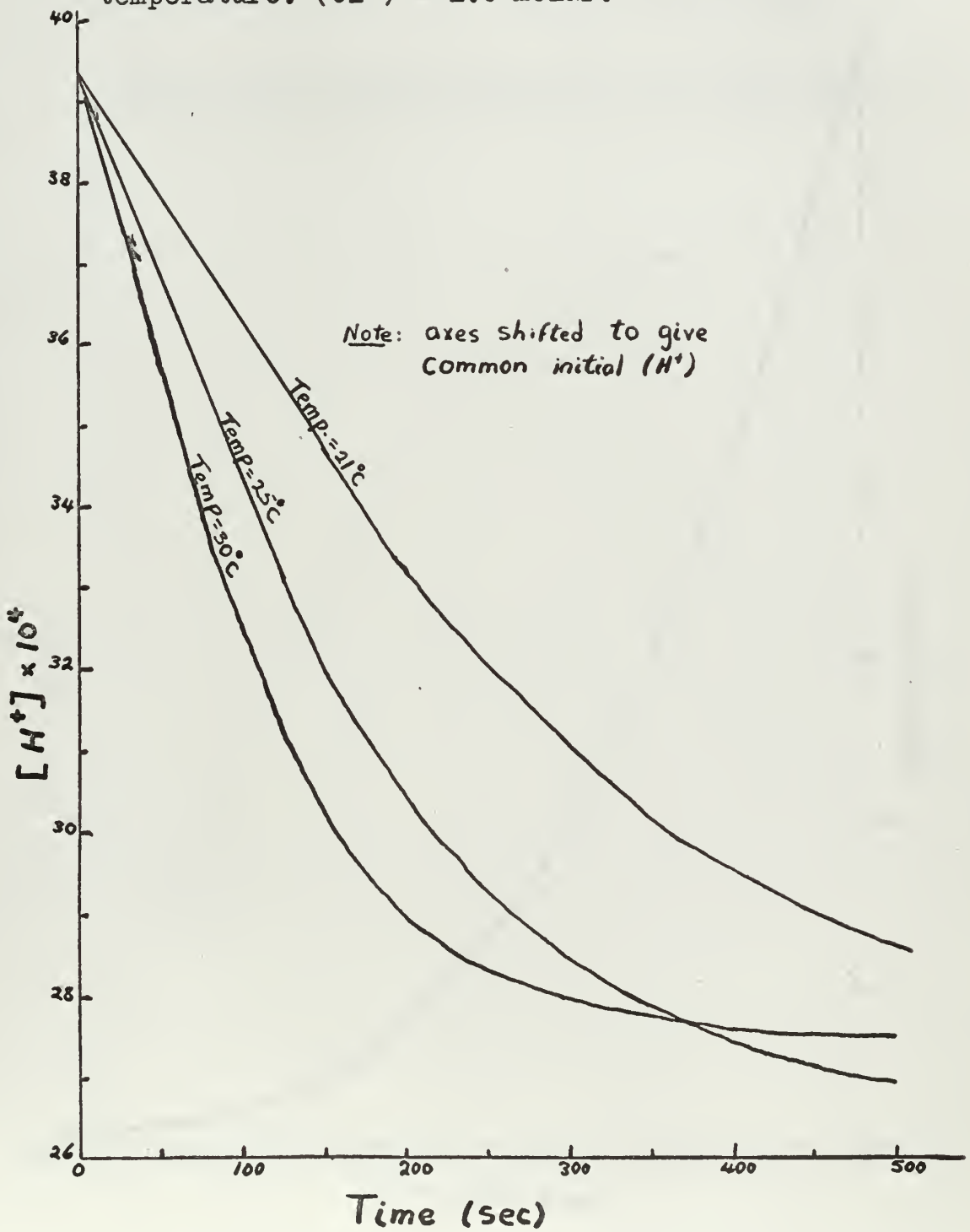


Figure 6a

Plot of absorbance versus time for a wavelength of 300 mμ. Pd= .00076M, (Cl^-) = 1.0, Temp.= 25°C.

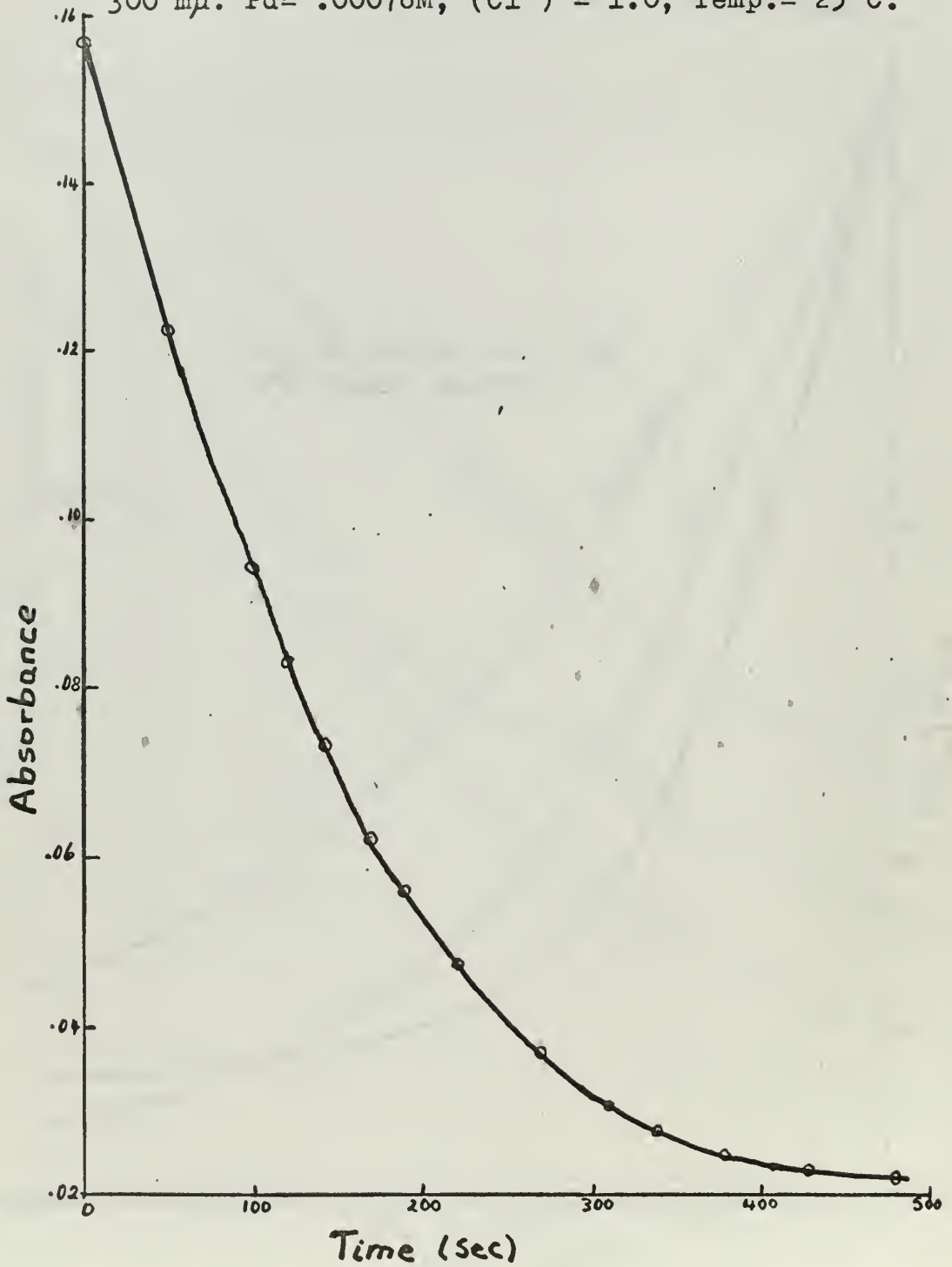
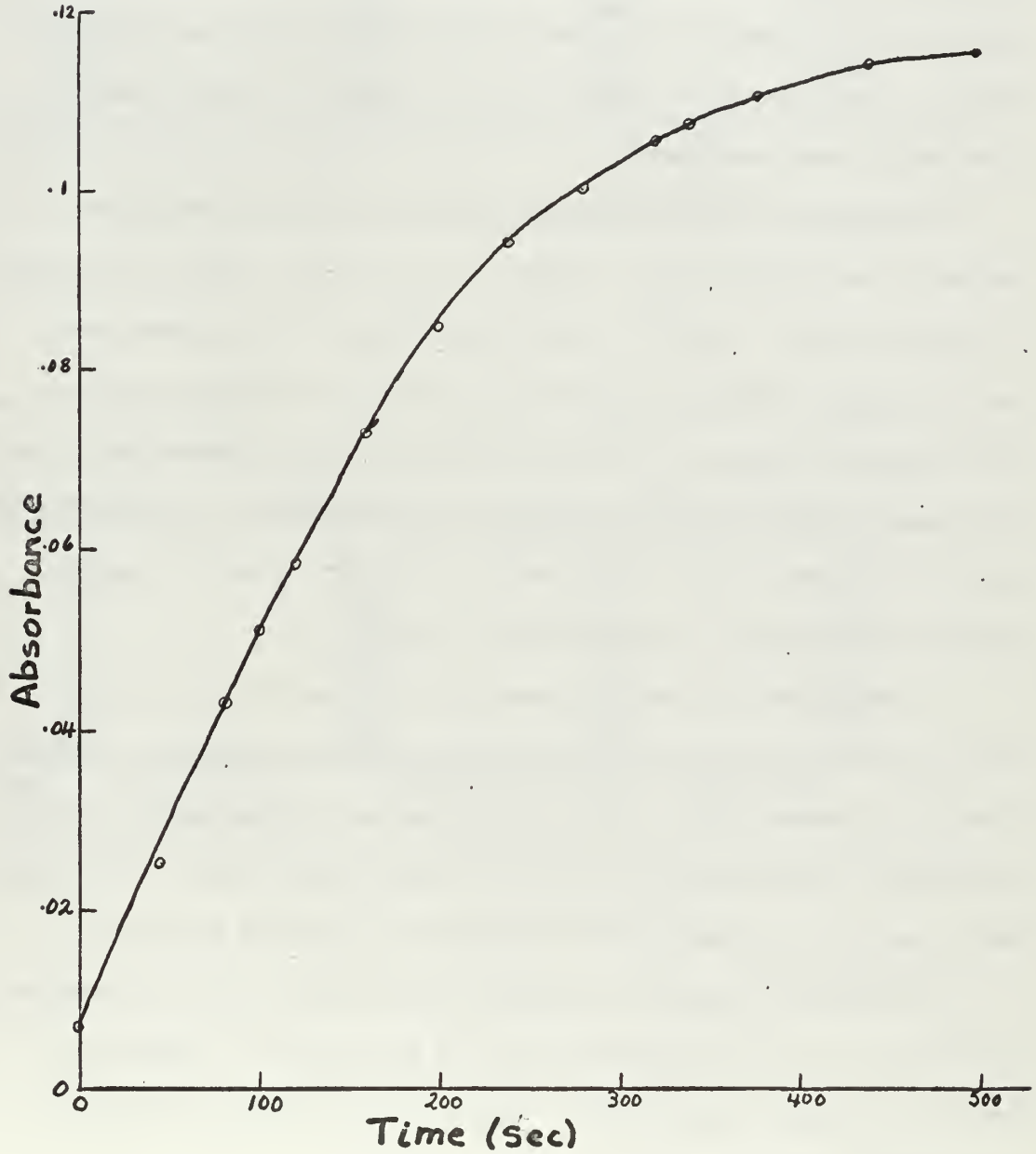


Figure 6b

Plot of absorbance versus time for a wavelength of 380 mμ. Pd= .00076M, (Cl^-) = 1.0, Temp.= 25°C.



6. Treatment of data.

Equilibrium quotient determination

An examination of the data of Table 3 reveals that the measurements of Table 3c vary slightly from the other two. These data were among the first taken and whether the inexperience of the author or other factors are involved cannot be determined. However, they represent actual measurements and since differences in both absorbances and pH values are involved in the calculation, any errors may cancel. The other sets of data are consistent with other observations which have been made.

The values of pH are measured values and have not been converted to actual pH values. However, since $(H^+) = D(H^+)_m$ as defined in equation (37), $-\log(H^+) = -\log D - \log(H^+)_m$ and we see that using measure values of pH only represents a shift in the pH coordinate. The conversion factor, D, will be eliminated when differences in pH are used. It was, therefore, decided to use measured values of pH and (H^+) to make initial calculations of K_1 and K_2 and to apply a correction directly to equations (12) and (13).

Substitution of data into equations (20) and (21) to obtain the uncorrected values of K_1 and K_2 was effected through the computer program of Appendix III. Points close to the maximum were not used since small deviations would result in very large errors. The values of K_1 and K_2 calculated in this manner are presented in Table 7.

The computer program of Appendix IV was used to plot theoretical curves for various calculated values of K_1 and K_2 for comparison with the observed experimental curves. A sample of its output is presented in Figure 10.

Table 7

Evaluation of the uncorrected equilibrium quotients K_1 and K_2 from absorbance and pH measurements

From data of Table 3a: $A_4 = .0480$, $A_2 = .067$, $A_m = .1135$, $(H_m^+) = 1.770 \times 10^{-5}$, $pH_m = 4.752$

Measured pH	Absorbance	$K_1 \times 10^{-5}$	$K_2 \times 10^{-5}$
5.938	.063	1.03	.432
5.605	.077	1.16	.385
5.559	.081	1.18	.376
5.471	.084	1.16	.385
5.363	.089	.989	.451
5.251	.0945	.812	.549
5.080	1.048	.811	.550
3.853	.082	.724	.615
Mean: $K_1 = .983$ $\times 10^{-5}$ $K_2 = .468$		Standard deviation: $K_1 \times 10^{-5} = .162$ $K_2 = .086$	

From data of Table 3b: $A_4 = .040$, $A_2 = .056$, $A_m = .098$, $(H_m^+) = 1.990 \times 10^{-5}$, $pH_m = 4.700$

Measured pH	Absorbance	$K_1 \times 10^{-5}$	$K_2 \times 10^{-5}$
5.169	.0823	.667	.520
5.409	.072	1.00	.346
5.535	.0663	1.04	.333
5.759	.0572	.997	.348
6.029	.050	1.01	.343
3.998	.0775	1.00	.346
3.677	.0675	.888	.391
Mean: $K_1 = .943$ $\times 10^{-5}$ $K_2 = .375$		Standard deviation: $K_1 \times 10^{-5} = .121$ $K_2 = .062$	

Table 7 (continued)

From data of Table 3c: A_4 = .043, A_2 = .064, A_m = .116 (H_m^+) = 1.950×10^{-5}, pH_m = 4.710

Measured pH	Absorbance	$K_1 \times 10^{-5}$	$K_2 \times 10^{-5}$
6.024	.055	.846	.436
5.943	.0575	.889	.415
5.834	.0618	.983	.376
5.638	.0697	.899	.411
5.209	.097	1.05	.350
4.066	.092	.818	.451
3.884	.086	1.15	.321
Mean: K_1 = .952 $\times 10^{-5}$ K_2 = .392		Standard deviation: K_1 = .101 $\times 10^{-5}$ K_2 = .044	

The corrected values of K_1 and K_2 are determined by using the relationship $(H^+) = D(H^+)_m$, that is, we must divide the uncorrected equilibrium coefficients by a suitably determined value of D. In fact, a value for D should have been determined for each set of data since its value is not a constant and can vary slightly. Since this was not done, we can only use a value which experience showed to be quite representative of the system being used. We will use D = 1.09.

We see from equations (12) and (13) that, since $(NH_4) = (Cl^-)$, $K_1' = K_1$ and $K_2' = K_2$.

Finally, using the relationships defined in equations (8) and (9), we combine the values calculated for K_1' and K_2' with the value we determined for K_a to determine the values of the desired equilibrium coefficients K_1'' and K_2''.

The least uncertainty is considered to be found in values of K_1 and K_2 calculated from the data of Table 3(b). A new power supply was used on the DU Spectrophotometer for the determination of this data greatly improved performance was observed. An excellent fit to this data was observed for uncorrected values of 1.00×10^5 and $.346 \times 10^5$ for K_1 and K_2 respectively. Applying the values of D and K_a as described above gives values of $K_1'' = 4.4 \times 10^{-5}$ and $K_2'' = 1.5 \times 10^{-5}$

Determination of rate constants

To treat the time versus (H^+) data, a plot of measured (H^+) versus time was prepared for each run. Extrapolation of the curve to t=0 gives an initial measured value of $(H^+) = (H^+)_o$, while a partial plot of (H^+) versus reciprocal time, followed by extrapolation, gives a final value of $(H^+) = (H^+)_f$ corresponding to $t = \infty$.

$(H^+)_o-(H^+)_f$ then represents a measure of the total reaction so that the (H^+) and time corresponding to any percent of reaction can be determined.

In terms of the measured $(H^+)_m$ values,

$$\text{percent reaction} = \frac{(H^+)_o-(H^+)_m}{(H^+)_o-(H^+)_f} \times 100 \qquad (40)$$

In terms of the actual (H^+) values we need only substitute the relationship $(H^+) = D(H^+)_m$ into the equivalent of (40) and, since this relationship also applies to the values of $(H^+)_o$ and $(H^+)_f$, the conversion factor, D, will conveniently cancel leaving only equation (40).

The calculation of the rate constants was executed in accordance with the methods outlined in the introductory part of this topic. The computer program of Appendix V was used to evaluate K versus τ-values for various δ . A sample of the output is presented in Table 8. Similarly the computer program of Appendix VI was used to prepare values of K versus τ_2/τ_1 (actually log τ_2/τ_1 for the sake of convenience) for use with the time ratio method. A sample of the output is presented in Table 9.

Equation (40) was then used to determine the (H^+) corresponding to various percents of reaction. The corresponding times were then read directly from the (H^+) versus time plot. Various time ratios were then compared with the corresponding tau ratios of Table 9 to determine a suitable value for K. The pseudo first-order rate constants were then determined: from the quotient of corresponding τ/t values for k_1 and from the product Kk_1 for k_2.

The times corresponding to various percent reactions for the solutions of various (Cl^-), together with the values calculated for k_1 and k_2 are given in Table 10.

Table 10a

Evaluation of pseudo first-order rate constants from reaction time and equivalent tau values, Kappa = 2, (Cl^-) = .056 molar.

Percent Reaction	Tau values for Kappa = 2	Reaction Time (sec)	k_1 (sec^{-1})	k_2 (sec^{-1})
20	.366	146	.0025	.0050
25	.456	185	.0025	.0050
30	.548	226	.0024	.0048
35	.644	264	.0024	.0048
40	.744	304	.0024	.0048
45	.850	346	.0025	.0050
50	.962	391	.0025	.0050
55	1.084	439	.0025	.0050
60	1.218	504	.0024	.0048
65	1.366	560	.0024	.0048
70	1.553	626	.0025	.0050

Table 10b

Evaluation of pseudo first-order rate constants from reaction time and equivalent tau values, Kappa = 2, (Cl^-) = .102 molar.

Percent Reaction	Tau values for Kappa = 2	Reaction Time (sec)	k_1 (sec^{-1})	k_2 (sec^{-1})
20	.366	116	.0031	.0062
25	.456	148	.0031	.0062
30	.548	180	.0030	.0060
35	.644	214	.0030	.0060
40	.744	245	.0030	.0060
45	.850	278	.0031	.0062
50	.962	312	.0031	.0062
55	1.084	351	.0031	.0062
60	1.218	391	.0031	.0062
65	1.366	442	.0031	.0062
70	1.553	498	.0031	.0062

Table 10c

Evaluation of pseudo first-order rate constants from reaction time and equivalent tau values, Kappa = 2, (Cl^-) = .192 molar.

Percent Reaction	Tau values for Kappa = 2	Reaction Time (sec)	k_1 (sec^{-1})	k_2 (sec^{-1})
20	.366	89	.0041	.0082
25	.456	111	.0041	.0082
30	.548	136	.0040	.0080
35	.644	158	.0041	.0082
40	.744	185	.0040	.0080
45	.850	213	.0040	.0080
50	.962	238	.0040	.0080
55	1.084	268	.0040	.0080
60	1.218	300	.0041	.0082
65	1.366	334	.0041	.0082
70	1.553	376	.0041	.0082

Table 10d

Evaluation of pseudo first-order rate constants from reaction time and equivalent tau values, kappa = 2, C^-) = .237 molar.

Percent Reaction	Tau values for Kappa = 2	Reaction Time (sec)	k_1 (sec^{-1})	k_2 (sec^{-1})
20	.366	80	.0046	.0092
25	.436	102	.0045	.0090
30	.548	121	.0045	.0090
35	.644	143	.0045	.0090
40	.744	164	.0045	.0090
45	.850	184	.0046	.0092
50	.962	211	.0046	.0092
55	1.084	240	.0045	.0090
60	1.218	269	.0045	.0090
65	1.366	306	.0045	.0090
70	1.553	339	.0046	.0092

Since it appeared that the observed pseudo first-order rate constants were of the type

$$k_1 = k_3 + k_4(Cl^-) \qquad (41)$$

a plot of calculated values of k_1 versus (Cl^-) was made and the linear plot of Figure 7 resulted. From the plot, the intercept was found to be = .0019 while the slope = .0112. In terms of the specific rate constants of equation (41), k_3 = .0019 sec^{-1} and k_4 = .0112 $\frac{liter}{sec\text{-}mole}$

It will be observed that a value of 2 was assigned to Kappa in all cases. An exact value of Kappa is very difficult to determine from experimental data and factors such as error in extrapolation, mixing time, and instrumental errors introduce a fair amount of uncertainty in its determination. An additional factor which must always be remembered for this system is that of reverse kinetics - a factor which can not be eliminated completely. A value of K = 2 appeared to this researcher to be a best choice. Examination of the slopes of the (H^+) versus time plots shows the plots to be very linear over approximately the first 60% of reaction for all values of (Cl^-), suggesting that very nearly the same value of Kappa obtains in all cases. The graphical method described in the introduction gives an excellent fit to the data for K = 2.

In order to treat the data of absorbance versus time, we must make the assumption that there is negligible accumulation of any intermediate species other than $Pd(NH_3)_3Cl^+$. If this assumption is valid, the concentrations of the individual species at any time may be determined from the relationships

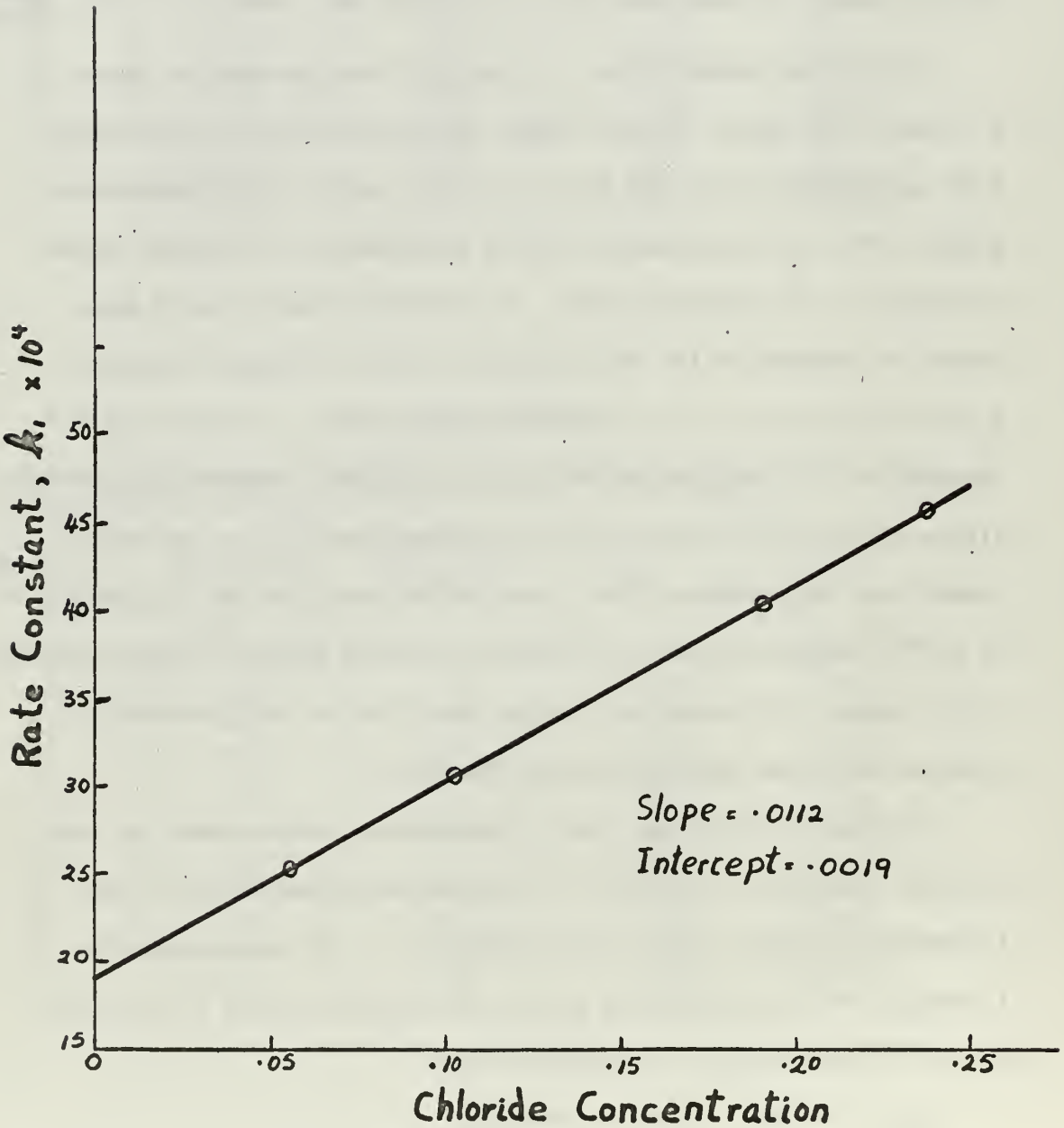
$$A_{300} = (a2Pd2 + a3Pd3 + a4Pd4)_{300}$$

$$A_{380} = (a2Pd2 + a3Pd3 + a4Pd4)_{380}$$

$$Pd2 + Pd3 + Pd4 = B$$

Figure 7

Plot of pseudo rate constants, k_1, versus (Cl^-)



where the 300 and 380 subscripts indicate the wavelength used. Other abbreviated terms are defined in the Table of Symbols.

The molar extinction coefficients a2 and a4 may be readily determined by direct measurement while the values for a3 can be calculated from equation (19) for each wavelength. The computer can be used to solve the above equations by Cramer's Method.

The pseudo first-order rate constants can be determined either by the time - percent reaction method or, since the concentrations of the individual species are available, by the direct solution of the integrated rate laws described by equations (30) and (31). This flexibility in the method of solving for the rate constants represents an advantage of absorbance-time measurements over (H^+)-time measurements since only the time - percent reaction method may be applied to the latter measurements.

Unfortunately, there was not sufficient time for this author to make a complete study of the kinetics of this system with time versus absorbance data. The limited measurements that were made proved valuable, however, in qualitatively determining the nature of the reaction mechanisms. Most of the absorbance at 300 $m\mu$ is due to Pd4 while most of the absorbance at 380 $m\mu$ is due to Pd2; therefore, a study of Figures 6a and 6b will give information about the rate of disappearance of Pd 4 and the rate of appearance of Pd2. We see, for instance, that the first substitution reaction is not fast compared to the second and that quite probably the second reaction is the faster of the two.

Absorbance-time measurements were also used to assess the contribution of reverse reaction kinetics to the observed reaction rate in acidic medium. Varying the (H^+) in NH_4^+ solution is equivalent

to varying the ammonia concentration. By varying the amount of acid added for successive absorbance-time determinations, it was possible to show that the contribution of reverse kinetics is insignificant over most of the reaction time. The plots of absrobance versus time obtained in this manner were almost identical for different (H^+) except for about the last 20 percent of the reaction when the rate decreased more rapidly for smaller (H^+).

Reverse kinetics

For constant (Cl^-) equations (8) and (9) may be written in the form

$$\frac{(Pd3)(NH_3)}{(Pd4)} = K_1^* , \qquad K_1^* = (Cl^-)K_1''$$

$$\frac{(Pd2)(NH_3)}{(Pd3)} = K_2^* , \qquad K_2^* = (Cl^-)K_2''$$

For the first substitution reaction it appears that at high (Cl^-), the forward rate = $k_1(Pd4)$ and the reverse rate = $k_{-1}(Pd3)(NH_3)$ which rearranges to give

$$\frac{(Pd3)(NH_3)}{(Pd4)} = \frac{k_1}{k_{-1}} = K_1^* \tag{42}$$

By analogy,

$$\frac{k_2}{k_{-2}} = K_2^* \tag{43}$$

The values of Table 11 were calculated from equations (42) and (43) using the values determined for K_1'' and K_2'' and the values of Table 10.

Table 11

Values of the reverse reaction rate constants. Temperature = 25°C

(Cl^-)	$\frac{1}{(Cl^-)}$	$K^*_{1\ x\ 10^6}$	$K^*_{2\ x\ 10^6}$	$k_{-1\ x10^{-3}}$	$k_{-2\ x\ 10^{-3}}$
.056	17.85	2.46	.84	1.0	5.83
.109	9.80	4.50	1.53	.68	4.05
.192	5.20	8.45	2.88	.48	2.81
.237	4.21	10.45	3.56	.433	2.54

Note: no corrections have been applied for differences in ionic strength

Plots of k_{-1} and k_{-2} versus $1/(Cl^-)$ were prepared and revealed linear relationships. The intercepts were 2.6×10^2 and 1.5×10^3 while the slopes were 4.2×10^1 and 2.5×10^2 for k_{-1} and k_{-2} plots respectively.

If we assume relationships of the type

$$k_{-1} = k_5 + \frac{k_6}{(Cl^-)} \qquad \text{and } k_{-2} = k_7 + \frac{k_8}{(Cl^-)}$$

then, $k_5 = 2.6 \times 10^2 \ \frac{\text{liter}}{\text{sec-mole}}$, $k_6 = 4.2 \times 10^1 \ \text{sec}^{-1}$,

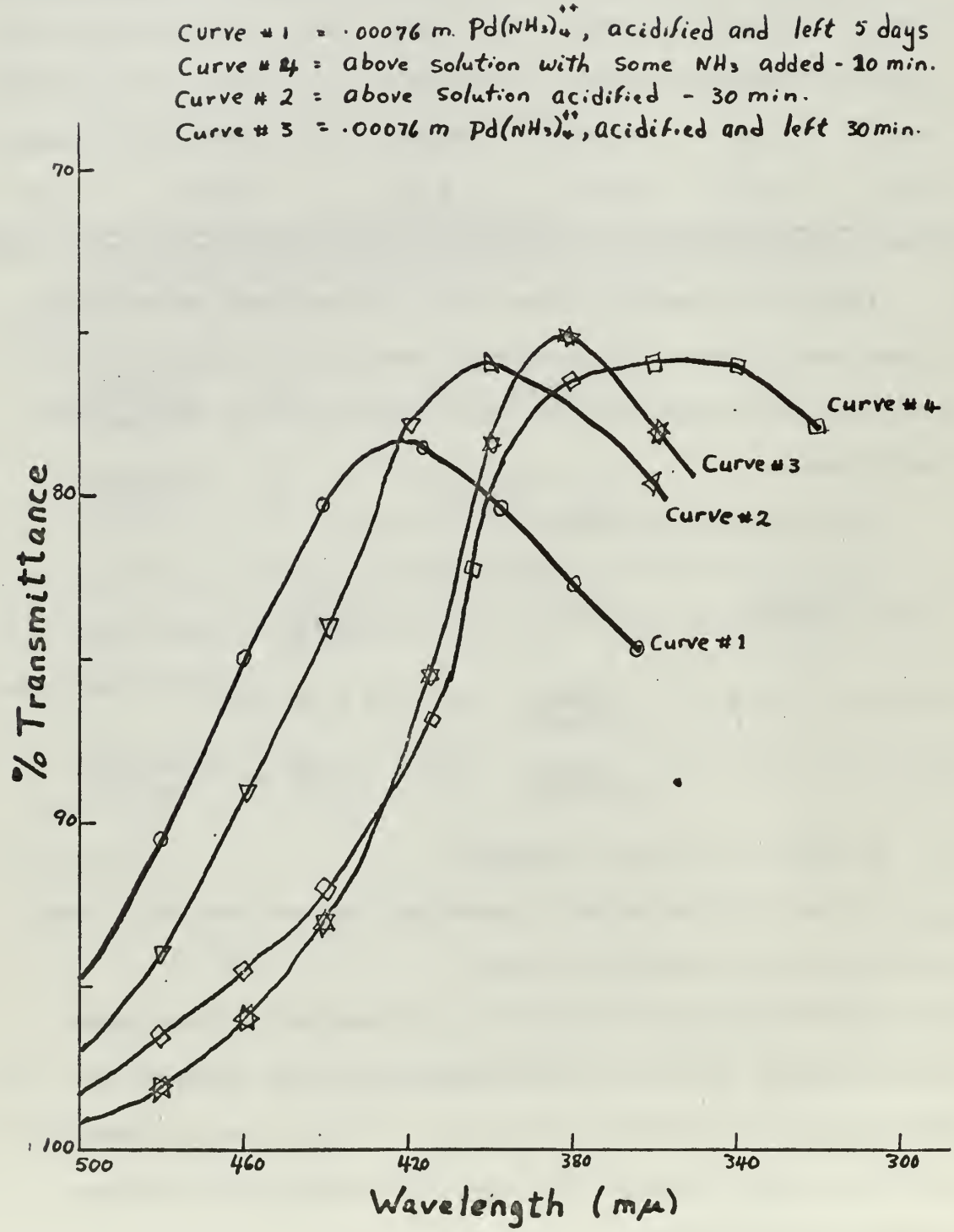
$k_7 = 1.5 \times 10^3 \ \frac{\text{liter}}{\text{mole-sec}}$, $k_8 = 2.5 \times 10^2 \ \text{sec}^{-1}$.

7. Evidence of cis-trans isomerism.

The data for the percent transmittance versus wavelength scans of Figure 8 was obtained as follows:

(1) Curve #1 represents the scan of a solution of 50 ml of .00076 molar $Pd(NH_3)_4^{++}$ which had been acidified with 5 ml of dilute HCl and allowed to equilibrate for 5 days. The scan reveals a maximum at 430 $m\mu$ which suggests that much of the complex has been converted to $Pd(NH_3)(Cl)_3^-$

Figure 8


Curve # 1 = .00076 m. $Pd(NH_3)_4^{++}$, acidified and left 5 days
Curve # 4 = above solution with some NH_3 added - 10 min.
Curve # 2 = above solution acidified - 30 min.
Curve # 3 = .00076 m $Pd(NH_3)_4^{++}$, acidified and left 30 min.
70
80
90
100
% Transmittance
500
460
420
380
340
300
Wavelength (mμ)
Curve # 4
Curve # 3
Curve # 2
Curve # 1

(2) Curve #4 represents the scan of the above solution after dilute ammonia had been carefully added. Presumably much of the complex would be in the form of $Pd(NH_3)_2Cl_2$ and $Pd(NH_3)_3Cl^+$ (maximum absorption at approximately 385 and 330 mμ respectively).

(3) Curve #2 represents the scan of the above solution approximately 30 minutes after it had been again acidified with HCl. We see that at least some of the complex has been again converted to $Pd(NH_3)(Cl)_3^-$ or $Pd(Cl)_4^{--}$.

(4) Curve #3 represents the scan for the original acidified $Pd(NH_3)_4^{++}$ solution just 30 minutes after the acid had been added. A second scan another 30 minutes later revealed virtually no change in this curve.

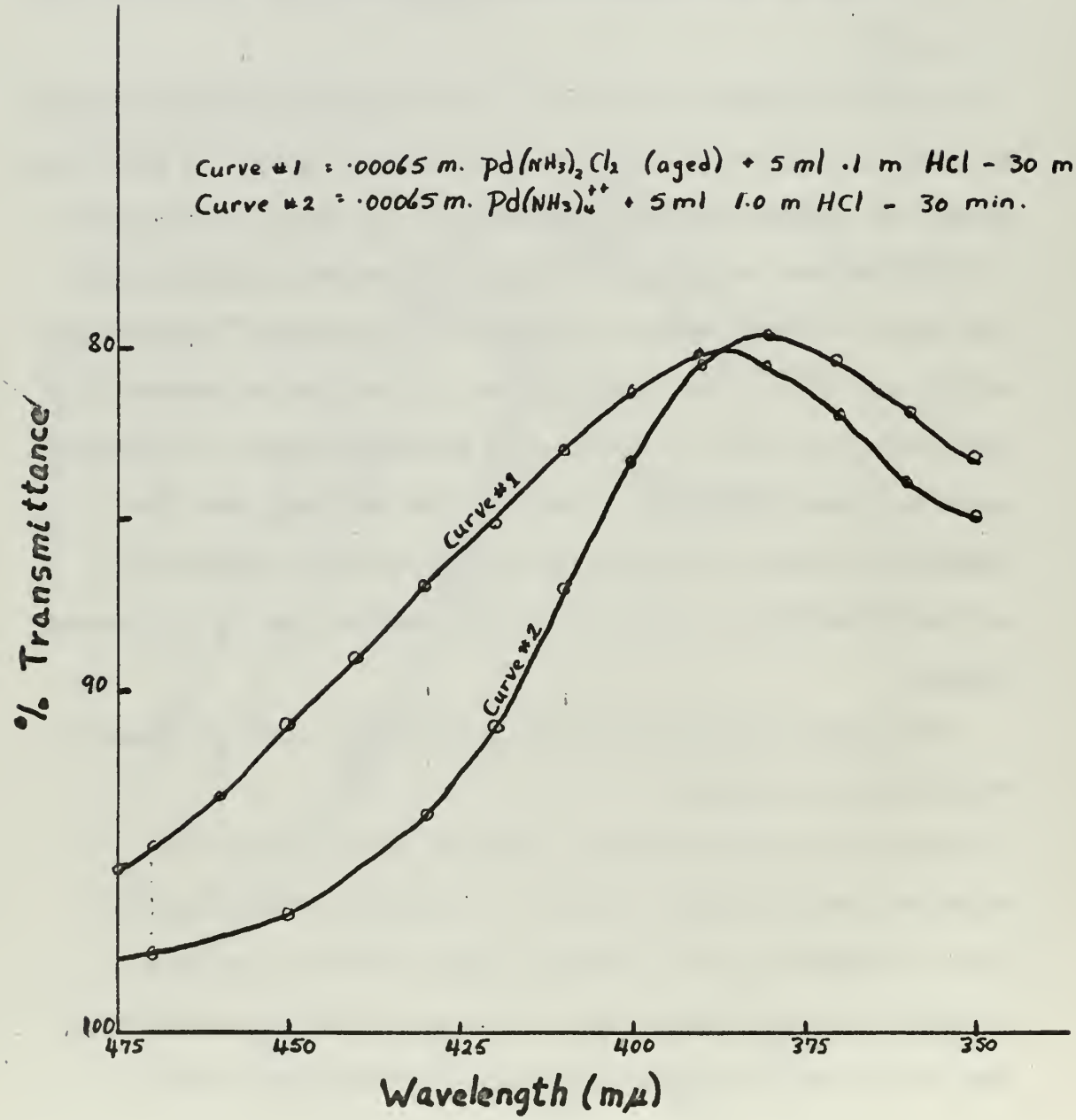
The explanation proposed to explain these observations is that the initial product achieved by adding HCl to $Pd(NH_3)_4^{++}$ solution is $Pd(NH_3)_2Cl_2$ of the trans configuration. It is further proposed that when ammonia is added as in the above described manner to a solution containing some $Pd(NH_3)Cl_3^-$ or $PdCl_4^{--}$, that at least some cis-$Pd(NH)_3Cl_2$ isomer is formed and that this isomer is subject to a more rapid substitution with Cl^- in HCl solution than is the trans species.

The percent transmittance versus wavelength scans of Figure 9 were prepared as follows:

(1) Curve #1 represents the scan taken 30 minutes after 5 ml of .1 molar HCl had been added to 50 ml of a solution which was .00065 molar in $Pd(NH_3)Cl_2$ and 1.0 molar in NH_4Cl and which had been allowed to age for several days. It appears from this scan that some of the complex has been converted to $Pd(NH_3)Cl_3^-$ or $PdCl_4^{--}$.

Figure 9

Plots of %transmittance versus wavelength



(2) Curve #2 represents the scan taken 30 minutes after 5 ml of 1.0 molar HCl had been added to a solution which was identical to (1) above except that the complex was initially in the form of $Pd(NH_3)_4^{++}$.

The explanation proposed for these observations is that the aged $Pd(NH_3)_2Cl_2$ had both cis and trans isomers present in equilibrium. Again, it appears from curve #2 that addition of HCl to $Pd(NH_3)_4^{++}$ results in the formation of only the trans isomer. That is, the initial product is kinetically determined while thermodynamic factors determine that eventually some cis isomer is formed. Martin et al[20] observed this type of phenomenon in studies of the substitution reactions of trichloroammine platinate(II) ion. Further scans of these solutions were made over a period of several days and it was observed that further chloride substitution proceeds very slowly. It is very probable that the rate of further substitution is determined by the rate of trans to cis isomerism. A very plausible mechanism for isomerism would be through the intermediate $Pd(NH_3)_3Cl^+$ species. Further study in this particular area though is required.

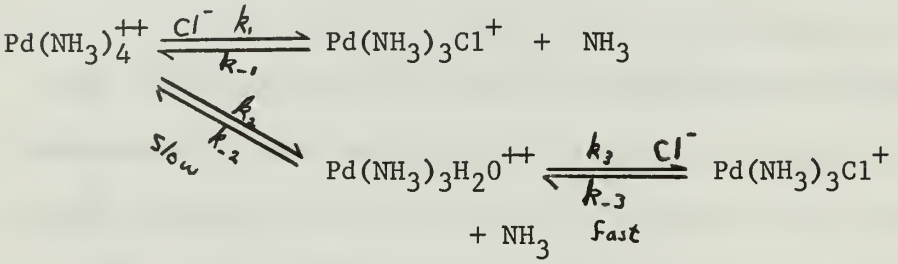
8. Proposed mechanism of substitution.

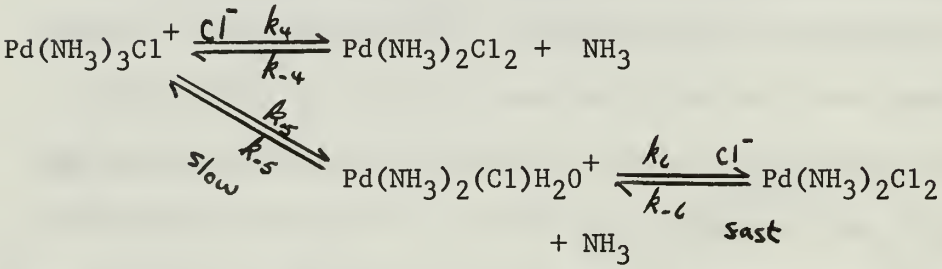
The results from this kinetics study suggest that the substitution reactions studied involve parallel mechanisms: one, a SN2 mechanism for the attack of Cl^- on the complex molecule and, the other, the attack of H_2O on the complex followed by a rapid elimination of the H_2O with replacement by Cl^-. The apparent insensitivity to charge as evidenced from the equilibrium quotients and the rate constants suggest that bond making and breaking are

[20]Tucker, Mary Ann, C. B. Colfin, and D. S. Martin, Jr., Inorg. Chem., 3, 1373, 1964

both important in the transition state. This correlates with our assumption that the chloride-independent term in the forward rate constants is indeed indicative of H_2O molecules being directly involved.

The following mechanisms are proposed:





Using the values calculated for the rate constants it is proposed that the rate constants for the proposed mechanism have the following values at 25°C:

$k_1 = .011 \frac{\text{liter}}{\text{mole-sec}}$ $\qquad k_{-1} = 2.6 \times 10^2 \frac{\text{liter}}{\text{mole-sec}}$

$k_2 = .0019 \text{ sec}^{-1}$ $\qquad k_{-2}k_{-3}/k_3 = 4.2 \times 10^1 \text{ sec}^{-1}$

$k_4 = .022 \frac{\text{liter}}{\text{mole-sec}}$ $\qquad k_{-4} = 1.5 \times 10^3 \frac{\text{liter}}{\text{mole-sec}}$

$k_5 = .0038 \text{ sec}^{-1}$ $\qquad \frac{k_{-5}k_{-6}}{k_6} = 2.5 \times 10^2 \text{ sec}^{-1}$

On the basis of this study it is further proposed that the trans effect is operative for these substitution reactions. The more rapid attack of Cl^- on $Pd(NH_3)_3Cl^+$ with its +1 charge than on $Pd(NH_3)_4^{++}$ with a charge of +2 suggests that the Cl^- ligand has a labilizing effect

on the ligand trans to it. The reverse kinetics show a similar trend with the substitution of NH_3 apparently proceeding more rapidly for the trans-$Pd(NH_3)_2Cl_2$ than for $Pd(NH_3)_3Cl^+$.

Figure 10

Plot of calculated absorbance vs pH: output of Appendix IV.

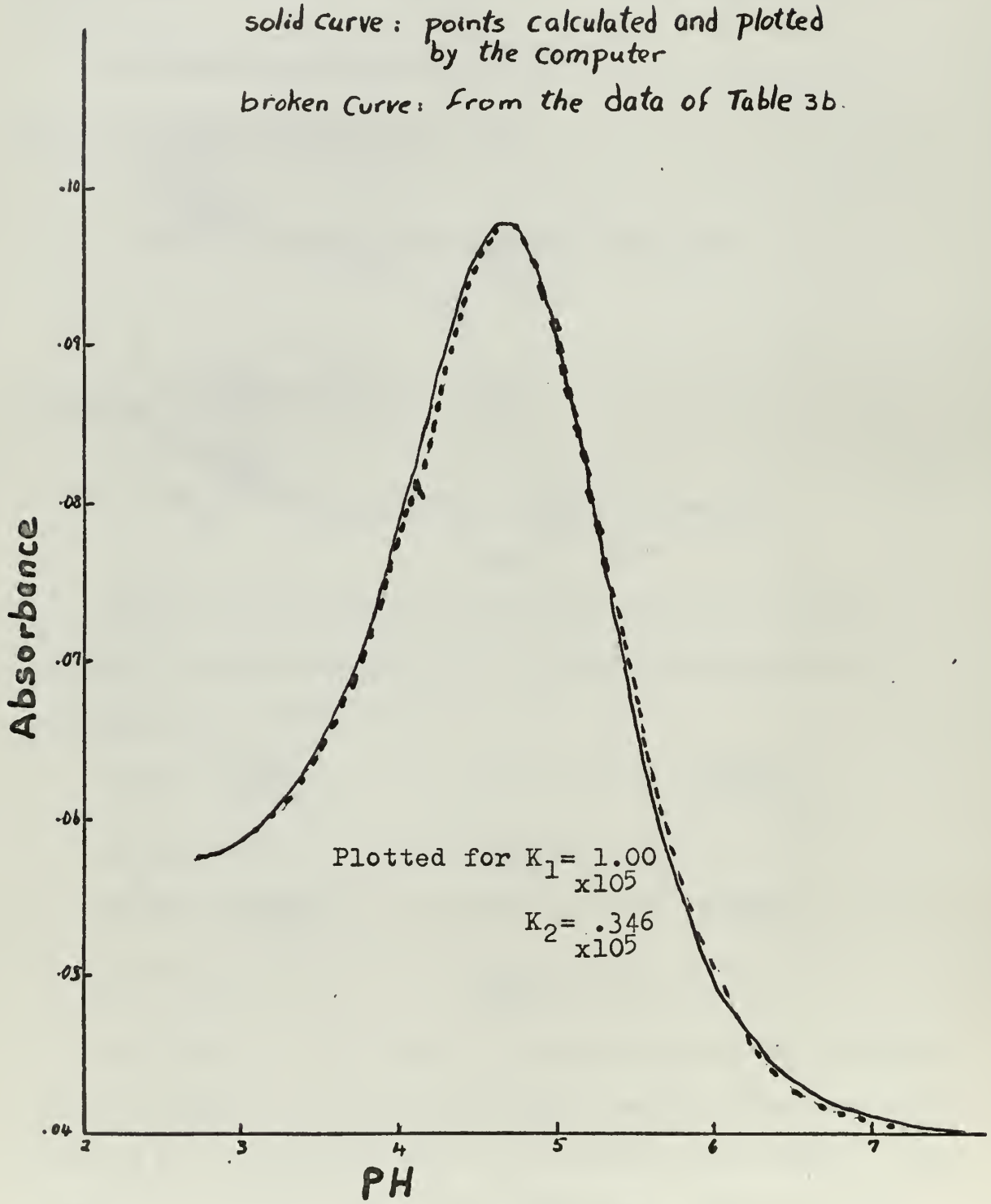


Table 2

Data for the determination of acidity quotient of ammonium ion. Increments of .01550 molar NH_3 added to 50.0 ml 1.0 molar NH_4Cl solution at 25°C.

Volume of NH_3 Added (ml)	Measured Hydrogen Ion Concentration x 10^7	Reciprocal Volume Added (ml^{-1})
0	187.9	
.823	17.78	1.215
1.463	9.817	.684
2.990	4.786	.334
4.610	3.141	.217
6.361	2.254	.157
7.786	1.841	.128
	Run #2	
.659	20.23	1.517
1.249	11.17	.801
2.894	4.887	.345
4.633	3.034	.216
6.528	2.148	.153
9.183	1.545	.109

Table 1

Data for determination of correction factor for conversion of measured (H^+) to actual (H^+). Increments of .0163 molar HCl added to 50.0 ml 1.0 molar NH_4Cl solution at 25°C.

Volume of HCl Added (ml)	Measured Hydrogen Ion Concentration x 10^4	Product of Total Volume and measured (H^+) (Ml - moles/liter) x 10^3
.350	.6699	3.374
.939	1.786	9.098
1.981	3.714	19.31
2.986	5.495	29.26
4.663	8.299	45.36
	Run #2	
.605	1.114	5.637
1.267	2.339	11.99
3.150	5.715	30.37
4.791	7.482	40.55
4.888	8.630	47.37

Table 3a

pH versus absorbance data at 25°C for (Pd) = .000760 molar

Measured pH	Absorbance	Measured pH	Absorbance
7.381	.0485	4.705	.112
6.381	.0525	4.593	.109
6.159	.054	4.557	.108
5.938	.063	4.542	.107
5.605	.077	4.353	.100
5.571	.078	3.981	.0855
5.559	.081	3.853	.082
5.471	.084	3.507	.075
5.363	.089	3.287	.071
5.251	.0945	3.274	.0705
5.080	1.048	3.025	.068
4.979	.108	2.886	.067
4.940	.110	2.594	.067
4.896	.112		
4.738	.1125		
4.726	.113		

Table 3b

pH versus absorbance data at 25°C for (Pd) = .000625 molar

Measured pH	Absorbance	Measured pH	Absorbance
7.631	.040	4.755	.0975
6.339	.0415	4.741	.0935
6.183	.0454	4.681	.0962
6.029	.050	4.616	.0958
5.759	.0572	4.452	.091
5.535	.0663	4.258	.084
5.409	.072	3.998	.0775
5.169	.0823	3.677	.0675
4.966	.091	3.459	.064
4.828	.0945	2.330	.056

Table 3c

pH versus absorbance data at 25°C for (Pd) = .000805 molar

Measured pH	Absorbance	Measured pH	Absorbance
7.468	.043	4.713	.1153
6.945	.043	4.669	.1135
6.488	.046	4.657	.113
6.236	.049	4.437	.110
6.144	.051	4.387	.106
6.024	.055	4.292	.102
5.943	.0575	4.066	.092
5.834	.0618	3.916	.0872
5.638	.0697	3.884	.086
5.466	.080	3.812	.082
5.209	.097	3.283	.070
5.134	.1035	3.180	.067
5.032	.107	2.774	.065
4.951	.110	2.530	.064
4.892	.111	2.396	.064
4.772	.112		

Table 4a

Time versus (H^+) measurements. Temperature = 25°C, (Cl^-) = .056 molar

Time (Seconds)	Hydrogen Ion Concentration x 10^4	Time (Seconds)	Hydrogen Ion Concentration x 10^4
0 (run #1)	46.42*	0 (run #2)	50.45*
80	44.06	80	48.42
100	43.95	100	48.31
120	43.65	120	48.08
140	43.15	140	47.64
160	42.85	160	47.21
180	42.46	180	46.88
200	41.98	200	46.45
220	41.50	220	46.03
240	41.11	240	45.50
260	40.64	260	45.08
280	40.18	280	44.67
300	39.72	300	44.16
340	38.90	340	43.45
380	38.11	380	42.66
420	37.41	420	42.07
460	36.73	460	41.30
500	36.14	500	40.83
540	35.48	540	40.18
580	34.99	580	39.72
620	34.59	620	39.17
700	33.57	700	38.19
800	32.66	800	37.33
900	31.92	900	36.64
1000	31.48	1000	35.97
1200	30.76	1200	35.16
1400	30.27	1400	34.75
1600	30.06	1700	34.28
2000	29.65	2000	34.04
	29.60*		34.00*

*Value obtained by extrapolation

Table 4b

Time versus (H^+) measurements. Temperature = 25°C, (Cl^-) = .102 molar

Time (Seconds)	Hydrogen Ion Concentration x 10^4	Time (Seconds)	Hydrogen Ion Concentration x 10^4
0	48.95*		51.20*
60	45.60	80	48.19
80	45.39	100	47.86
100	45.08	120	47.42
120	44.46	100	46.34
140	43.95	180	45.71
160	43.35	200	45.13
180	42.66	220	44.62
200	42.04	240	44.06
220	41.50	260	43.45
240	40.79	280	42.85
260	40.18	300	42.36
300	38.99	320	41.88
340	38.02	340	41.40
380	37.07	360	40.93
420	36.22	380	40.46
460	35.40	400	40.04
500	34.73	420	39.63
540	34.12	440	39.31
580	33.50	460	38.99
620	33.08	500	38.32
660	32.58	580	37.24
700	32.14	620	36.81
740	31.77	700	36.01
800	31.33	800	35.24
900	31.48	900	34.67
1100	29.99	1000	34.28
1300	29.51	1200	33.73
1600	29.17	1400	33.37
2000	28.97	1600	33.19
	28.9 *	2000	33.10
			32.90*

*Value obtained by extrapolation

Table 4c

Time versus (H^+) measurements. Temperature = 25°C, (Cl^-) = .192 molar

Time (Seconds)	Hydrogen Ion Concentration x 10^4	Time (Seconds)	Hydrogen Ion Concentration x 10^4
0	56.0 *	0	56.3 *
80	51.40	80	52.12
100	50.93	100	51.71
120	50.23	120	50.93
140	49.43	140	50.12
160	48.53	160	49.20
180	47.64	180	48.42
200	46.88	200	47.53
220	46.09	220	46.81
240	45.29	240	45.92
260	44.57	260	45.19
280	43.85	280	44.46
300	43.15	300	43.85
320	42.66	320	43.35
340	42.03	340	42.85
360	41.50	360	42.27
380	41.07	380	41.69
400	40.51	400	41.21
440	39.81	420	40.74
480	39.08	440	40.31
520	38.37	500	39.29
560	37.76	620	37.76
600	37.33	700	37.07
700	36.31	800	36.35
800	35.78	1000	35.56
1000	34.99	1200	35.29
1200	34.91	1400	35.05
1400	34.80		35.00*
	34.70*		

* Value obtained by extrapolation

Table 4d

Time versus (H^+) measurements. Temperature = 25°C, (Cl^-) = .237 molar

Time (Seconds)	Hydrogen Ion Concentration x 10^4	Time (Seconds)	Hydrogen Ion Concentration x 10^4
0	30.20*	400	13.96
60	26.61	440	13.24
80	25.79	480	12.59
100	24.83	560	11.61
120	23.77	600	11.22
140	22.91	700	10.45
160	21.88	800	9.95
180	20.91	900	9.59
200	20.18	1000	9.34
240	18.54	1100	9.20
280	17.14	1200	9.12
320	15.96	1300	9.04
360	14.93	1400	8.99

*Value obtained by extrapolation

Table 5a

Time versus (H^+) measurements. Temperature = 21°C, 1.0 molar in NH_4Cl

Time (Seconds)	Hydrogen Ion Concentration x 10^4	Time (Seconds)	Hydrogen Ion Concentration x 10^4
60	37.38	60	34.75
80	36.81	80	34.32
100	36.31	100	33.61
120	35.71	120	32.91
140	34.99	140	32.18
160	34.36	160	31.62
180	33.81	180	30.90
200	33.27	200	30.31
220	32.81	220	29.85
240	32.21	240	29.27
280	31.45	280	28.44
320	30.69	320	27.67
360	29.99	360	27.10
400	29.51	400	26.55
440	29.11	440	26.06
480	28.71	480	25.74
540	28.25	540	25.23
700	27.61		
800	27.23		
900	26.98		
1020	26.79		
1160	26.61		

Table 5b

Time versus (H^+) measurements. Temperature = 25°C, 1.0 molar in NH_4Cl

Time (Seconds)	Hydrogen Ion Concentration x 10^4	Time (Seconds)	Hydrogen Ion Concentration x 10^4
60	31.84	60	35.20
80	30.69	80	34.12
100	29.79	100	33.11
120	28.84	120	32.21
140	28.12	140	31.33
160	27.29	160	30.62
180	26.61	180	29.92
200	26.06	200	29.26
220	25.59	220	28.77
240	25.06	240	28.35
280	24.38	280	27.67
320	23.88	320	27.10
360	23.47	360	26.61
400	23.17	400	26.20
440	22.93	440	26.06
480	22.75	480	25.88
540	22.54	540	25.70
660	22.31	700	25.47
760	22.24		
960	22.18		

Table 5c

Time versus (H^+) measurements. Temperature = 30°C, 1.0 molar in NH_4Cl

Time (Seconds)	Hydrogen Ion Concentration x 10^4	Time (Seconds)	Hydrogen Ion Concentration x 10^4
60	36.22	60	39.08
100	33.50	80	37.67
120	32.63	100	36.56
140	31.92	120	35.54
160	31.41	140	34.83
180	30.90	160	34.28
200	30.59	180	33.73
220	30.41	200	33.42
240	30.06	220	33.11
280	29.82	240	32.85
320	29.65	280	32.58
360	29.54	320	32.28
400	29.49	360	32.20
440	29.42	400	32.07
480	29.39	440	32.04
540	29.44	480	32.02
		540	31.99

Table 6a

Time versus absorbance measurements for a wavelength of 300 mμ. Palladium concentration = .00076 molar, temperature = 25°C, solution 1.0 molar in NH_4Cl

Time (Seconds)	Absorbance	Time (Seconds)	Absorbance
0	.157	0	.157
45	.128	50	.1225
75	.1055	100	.0945
100	.0925	120	.083
120	.082	140	.074
140	.0715	170	.0625
160	.0625	190	.0565
190	.0535	220	.0475
220	.0455	270	.0375
250	.0383	310	.031
280	.033	340	.0280
340	.025	380	.025
380	.022	430	.023
		480	.022

Table 6b

Time versus absorbance measurements for a wavelength of 380 mμ. Palladium = .00076 molar, temperature = 25°C, solution 1.0 molar in NH_4Cl.

Time (Seconds)	Absorbance	Time (Seconds)	Absorbance
0	.0069	0	.0069
45	.025	60	.026
60	.032	90	.046
80	.043	110	.055
100	.051	130	.0625
120	.0595	150	.070
140	.066	170	.076
160	.073	190	.082
180	.0795	220	.090
200	.0847	260	.0975
240	.094	300	.1025
280	.1005	340	.1075
320	.105	380	.111
340	.1075	420	.114
380	.1105	450	.115
440	.114	500	.116
500	.115		

Table 8

Tau versus kappa values for various percent reaction

Kappa	tau 15	tau 16	tau 17	tau 18	tau 19
1.10000	.30221	.32248	.34284	.36332	.38390
1.20000	.29736	.31739	.33749	.35767	.37793
1.30000	.29427	.31395	.33368	.35348	.37335
1.40000	.29136	.31071	.33010	.34954	.36905
1.50000	.28860	.30763	.32671	.34583	.36500
1.60000	.28596	.30472	.32350	.34231	.36117
1.70000	.28345	.30194	.32044	.33898	.35755
1.80000	.28106	.29929	.31754	.33581	.35412
1.90000	.27877	.29677	.31477	.33280	.35086
2.00000	.27657	.29435	.31213	.32993	.34775
2.10000	.27447	.29204	.30961	.32719	.34479
2.20000	.27244	.28982	.30719	.32457	.34196
2.30000	.27050	.28769	.30487	.32206	.33926
2.40000	.26863	.28564	.30265	.31965	.33667
2.50000	.26683	.28368	.30051	.31734	.33419
2.60000	.26510	.28178	.29845	.31513	.33181
2.70000	.26342	.27996	.29647	.31299	.32952
2.80000	.26181	.27819	.29457	.31094	.32732
2.90000	.26024	.27649	.29273	.30896	.32520
3.00000	.25873	.27485	.29095	.30705	.32316
3.10000	.25727	.27326	.28924	.30521	.32120
3.20000	.25585	.27172	.28758	.30343	.31930
3.30000	.25448	.27023	.28597	.30171	.31746
3.40000	.25314	.26879	.28442	.30005	.31569
3.50000	.25185	.26739	.28292	.29844	.31397
3.60000	.25059	.26603	.28146	.29688	.31231
3.70000	.24937	.26471	.28004	.29537	.31070
3.80000	.24819	.26343	.27867	.29390	.30914
3.90000	.24703	.26219	.27733	.29248	.30763
4.00000	.24591	.26098	.27604	.29109	.30616
4.10000	.24482	.25980	.27478	.28975	.30474
4.20000	.24375	.25866	.27355	.28845	.30336
4.30000	.24272	.25754	.27236	.28718	.30201
4.40000	.24171	.25646	.27120	.28594	.30071
4.50000	.24072	.25540	.27007	.28474	.29943
4.60000	.23976	.25437	.26897	.28357	.29820
4.70000	.23882	.25336	.26789	.28243	.29699
4.80000	.23790	.25238	.26685	.28132	.29582
4.90000	.23701	.25142	.26583	.28024	.29468
5.00000	.23613	.25048	.26483	.27918	.29356
5.10000	.23528	.24957	.26386	.27815	.29248
5.20000	.23444	.24868	.26291	.27715	.29142
5.30000	.23363	.24781	.26198	.27617	.29038
5.40000	.23283	.24695	.26107	.27521	.28937
5.50000	.23205	.24612	.26019	.27427	.28839
5.60000	.23128	.24530	.25932	.27336	.28742
5.70000	.23054	.24450	.25848	.27246	.28648
5.80000	.22980	.24372	.25765	.27159	.28557
5.90000	.22908	.24296	.25684	.27074	.28467

Table 9

Log of time ratios for various percent reaction.

Kappa	$\log \frac{\tau_{70}}{\tau_{10}}$	$\log \frac{\tau_{70}}{\tau_{20}}$	$\log \frac{\tau_{70}}{\tau_{30}}$	$\log \frac{\tau_{70}}{\tau_{40}}$	$\log \frac{\tau_{70}}{\tau_{50}}$
1.100000	.950971	.649743	.464705	.325338	.208495
1.200000	.948443	.644967	.460829	.322612	.206810
1.300000	.941557	.640153	.457517	.320432	.205519
1.400000	.935600	.636153	.454849	.318732	.204547
1.500000	.930469	.632826	.452705	.317417	.203831
1.600000	.926037	.630060	.450993	.316418	.203323
1.700000	.922201	.627767	.449642	.315679	.202984
1.800000	.918877	.625873	.448592	.315156	.202785
1.900000	.915996	.624322	.447797	.314815	.202701
2.000000	.913500	.623064	.447219	.314625	.202714
2.100000	.911342	.622060	.446826	.314565	.202808
2.200000	.909481	.621277	.446593	.314614	.202969
2.300000	.907883	.620685	.446496	.314756	.203187
2.400000	.906517	.620261	.446518	.314977	.203452
2.500000	.905357	.619984	.446642	.315265	.203757
2.600000	.904382	.619836	.446854	.315611	.204094
2.700000	.903572	.619802	.447143	.316006	.204459
2.800000	.902909	.619867	.447498	.316442	.204847
2.900000	.902379	.620022	.447911	.316913	.205253
3.000000	.901968	.620254	.448374	.317414	.205673
3.100000	.901665	.620555	.448880	.317939	.206105
3.200000	.901458	.620917	.449422	.318485	.206546
3.300000	.901339	.621333	.449997	.319047	.206993
3.400000	.901298	.621797	.450599	.319623	.207445
3.500000	.901330	.622302	.451223	.320209	.207900
3.600000	.901425	.622844	.451868	.320804	.208356
3.700000	.901580	.623418	.452528	.321404	.208811
3.800000	.901787	.624021	.453202	.322009	.209265
3.900000	.902042	.624649	.453886	.322615	.209717
4.000000	.902341	.625297	.454579	.323222	.210166
4.100000	.902679	.625965	.455279	.323829	.210611
4.200000	.903053	.626648	.455983	.324434	.211051
4.300000	.903459	.627345	.456690	.325036	.211486
4.400000	.903894	.628054	.457399	.325635	.211916
4.500000	.904356	.628772	.458109	.326229	.212339
4.600000	.904841	.629498	.458817	.326818	.212756
4.700000	.905348	.630230	.459524	.327401	.213167
4.800000	.905875	.630967	.460229	.327979	.213571
4.900000	.906418	.631708	.460930	.328549	.213968
5.000000	.906977	.632452	.461627	.329113	.214358

APPENDIX I

Derivation of the equations for equilibrium quotient determination

For high chloride and ammonium ion concentrations, the equilibrium quotient expressions

$$\frac{(Pd(NH_3)_3Cl^+)(NH_4^+)}{(Pd(NH_3)_4^{++})(H^+)(Cl^-)} = K_1' \quad (1)$$

$$\frac{(Pd(NH_3)_2Cl_2)(NH_4^+)}{(Pd(NH_3)_2Cl^+)(H^+)(Cl^-)} = K_2' \quad (2)$$

may be written in the form

$$\frac{(Pd(NH_3)_4Cl^+)}{(Pd(NH_3)_4^{++})(H^+)} = K_1' \frac{(Cl^-)}{(NH_4^+)} = K_1 \quad (3)$$

$$\frac{(Pd(NH_3)_2Cl_2)}{(Pd(NH_3)_3Cl^+)(H^+)} = K_2' \frac{(Cl^-)}{(NH_4^+)} = K_2 \quad (4)$$

Using the abbreviations as defined in the Table of Symbols, (3) and (4) become

$$\frac{Pd_3}{Pd_4 (H^+)} = K_1 \quad (5)$$

$$\frac{Pd_2}{Pd_3 (H^+)} = K_2 \quad (6)$$

The absorbance of a solution containing these complex species is given by equation (7).

$$A = L(a_4 Pd4 + a_3 Pd3 + a_2 Pd2) \quad (7)$$

It is assumed here that no other species present absorb at the wavelength being used. a_4, a_3, and a_2 are the corresponding molar extinction coefficients and L = cell thickness.

Substitution of (5) and (6) into (7) gives

$$A = L\left[Pd_4 (a_4 + K_1 (H^+) a_3 + K_1K_2(H^+)^2 a_2) \right] \quad (8)$$

which, when divided by the total palladium concentration B, results in equation (9)

$$E = \frac{A}{BL} = \frac{a_4 + K_1(H^+)a_3 + K_1K_2(H^+)^2 a_2}{1 + K_1(H^+) + K_1K_2(H^+)^2} \qquad (9)$$

At a wavelength for which a_3 is larger than a_2 or a_4, a plot of E versus PH values will result in a curve such as Figure 1. Since the curve possesses a maximum, the derivative of equation (9) should locate this critical point. Thus

$$\frac{dE}{d(H^+)} = \frac{[1+K_1(H^+)+K_1K_2(H^+)^2][K_1a_3+2(H^+)K_1K_2a_2] - [a_4+K_1(H^+)a_3+K_1K_2(H^+)^2a_2][K_1+2(H^+)K_1K_2]}{[1+K_1(H^+)+K_1K_2(H^+)^2]^2} = 0$$

from which is obtained (10)

$$a_3 - a_4 + 2(H^+)K_2(a_2 - a_4) + (H^+)^2K_1K_2(a_2 - a_3) = 0 \qquad (10)$$

If E_m and (H_m^+) are the coordinates of the maximum, then, from (9)

$$E_m = \frac{a_4 + K_1(H_m^+)a_3 + K_1K_2(H_m^+)^2 a_2}{1 + K_1(H_m^+) + K_1K_2(H_m^+)^2} \qquad (11)$$

The value of a_3 from (10) is substituted into (11) to obtain an expression:

$$E_m[1+K_1(H_m^+)+K_1K_2(H_m^+)^2][1-(H_m^+)^2K_1K_2] = [a_4+K_1K_2(H_m^+)^2a_2][1-(H_m^+)^2K_1K_2] + K_1(H_m^+)[a_4-2(H_m^+)K_2(a_2-a_4) - (H_m^+)^2K_1K_2a_2]$$

which simplifies to equation (12)

$$(K_1K_2)^2(E_m-a_2)(H_m^+)^4+K_1K_2(H_m^+)^2(a_4-a_2-(H_m^+)Ka_2+(H_m^+)K_1E_m) + (K_1(H_m^+)+1)(a_4-E_m) = 0 \qquad (12)$$

Fortunately (12) factors into:

$$[K_1K_2(H_m)^2(E_m-a_2)+(a_4-E)][K_1K_2(H_m)^2+K_1(H_m^+)+1] = 0$$

Only the first factor gives a root with physical significance:

$$K_1K_2(H_m)^2(E_m - a_2) - (E_m - a_4) = 0$$

which may be written in the form

$$K_1K_2 = \frac{E_m - a_4}{(H_m)^2(E_m - a_2)} \tag{13}$$

Any point on the curve is defined by the functional relationship (9). Furthermore, the hydrogen ion concentration may be described with reference to (H_m^+),

$$(H^+) = (H_m^+)10^{-\Delta} \tag{14}$$

Where Δ equals the difference between the pH at the point and the pH at the maximum. Substituting (14) into (9) yields equation (15)

$$E = \frac{4 + K(H^+)10^{-\Delta}a_3 + K K (H^+)^2 10^{-2\Delta} a_2}{1 + K_1(H_m^+)10^{-\Delta} + K_1K_2(H_m^+)^2 10^{-2\Delta}} \tag{15}$$

Combining (15) with (11) so as to eliminate terms in a_3 results in equation (16)

$$K_1 = \frac{E_m - a_4)(E - a_2)10^{-\Delta} - 2(E_m - a_4)(E_m - a_2) + 10^{\Delta}(E - a_4)(E_m - a_2)}{(H)_m (E_m - a_2)(E_m - E)} \tag{16}$$

For most systems (13) and (16) may be written

$$K_1K_2 = \frac{A_m - A_4}{(H_m^+)(A_m - A_2)} \tag{17}$$

$$K_1 = \frac{(A_m - A_4)(A - A_2)10^{-\Delta} - 2(A_m - A_4)(A_m - A_2) + 10^{\Delta}(A - A_4)(A_m - A_2)}{(H_m^+)(A_m - A_2)(A_m - A)} \tag{18}$$

Where, as indicated on Figure 1, A_m and (H_m^+) are located at the maximum on the curve, A_4 is the minimum absorbance at low pH values. Any point on the curve yields a set of values for A and Δ. A is the absorbance and Δ is the difference between the pH at the point and the pH at the maximum.

APPENDIX II

Solution of the rate law differential equations for series first-order reactions

For the equations

$$A \xrightarrow{k_1} B \tag{1}$$

$$B \xrightarrow{k_2} C \tag{2}$$

the rate equations which obtain are

$$\frac{dA}{dt} = -k_1 A \tag{3}$$

$$\frac{dB}{dt} = k_1 A - k_2 B \tag{4}$$

$$\frac{dC}{dt} = k_2 B \tag{5}$$

(3) may be integrated immediately by separating variables and using the initial value A_o as the constant of integration to give

$$\ln A = k_1 t + \ln A_o \quad \text{or} \quad A = A_o e^{-k_1 t} \tag{6}$$

Substituting (6) into (4) yields (7)

$$\frac{dB}{dt} = k_1 A_o e^{-k_1 t} - k_2 B \tag{7}$$

which may be readily integrated by either using an integrating factor or by means of Laplace transforms. Using the latter method and assuming the initial value $B_o = 0$, the transformed equation is

$$SB(s) = \frac{k_1 A_o}{S+k_1} - k_2 B(s)$$

$$B(s) = \frac{k_1 A_o}{(S+K_1)(S+K_2)} = \frac{\frac{k_1 A_o}{k_2 - k_1}}{S+k_1} - \frac{\frac{k_1 A_o}{k_2 - k_1}}{S+k_2} \tag{8}$$

Transforming equation (8) into the time domain gives

$$B = \frac{k_1 A_o}{k_2 - k_1} \left(e^{-k_1 t} - e^{-k_2 t} \right) \tag{9}$$

The integrated form of (5) can be obtained simply from the stoichiometric relationship which must exist, that is

$$A + B + C = A_o$$

Assuming the initial value $C_o = 0$, and substituting values for A and B from (6) and (9) gives

$$C = A_o - B - C = A_o - A_o e^{-k_1 t} - \frac{k_1 A_o}{k_2 k_1} \left(e^{-k_1 t} - e^{k_2 t} \right)$$

$$= A_o \left[1 - \frac{k_2 e^{-k_1 t} + k_1 e^{-k_2 t}}{k_2 - k_1} \right] \tag{10}$$

$$= A_o \left[1 + \frac{1}{k_1 - k_2} \left(k_2 e^{-k_1 t} - k_1 e^{-k_2 t} \right) \right]$$

APPENDIX III

Computer program for calculating equilibrium quotients

```
      PROGRAM EQUILIB
      DIMENSION A(50),B(50)
      READ 3,N,C,D,X,Y,Z,(A(I),B(I),I=1,N)
    3 FORMAT (I2, 5F10.0/(2F10.0))
      G1=X-D
      G2=X-C
      G12=2.*G1*G2
      Q=G1/(G2*Y**2)
      DO 4 I=1,N
      DEL=B(I)-Z
      E=10.**DEL
      A(I)=((G1*(A(I)-C))/E-G12+(A(I)-D)*G2*E)/(Y*G2*(X-A(I)))
      B(I)=Q/A(I)
    4 CONTINUE
      PRINT 6,(A(I),B(I),I=1,N)
    6 FORMAT(3HK1=E20.8,3HK2=E20.8)
      STOP
      END
      END
```

Program input:

N = number of data points
C = A2
D = A_4
X = maximum absorbance
Y = (Hm^+)
Z = pHm
A = measured absorbances
B = measured pH values.

Program output:

K_1 = uncorrected equilibrium quotient defined by equation (12)

K_2 = uncorrected equilibrium quotient defined by equation (13)

APPENDIX IV

Computer program to plot absorbance versus pH curve for given values of K_1 and K_2.

```
      PROGRAM COMPARE
      DIMENSION X(50),Y(50),ITITLE(12)
      READ 3,A,B,D2,D4,H,D,C
    3 FORMAT(7F10.0)
      EP3=(D*(1.+A*H+A*B*H*H)-D4-D2*A*B*H*H)/(C*A*H)
      PH=2.7
      LABEL=4H
      DO 1 I=1,12
    1 ITITLE(I)=8H
      ITITLE(1)=8HJOB0462
      ITITLE(2)=8HSPARKES
      ITITLE(3)=8H R. K.
      ITITLE(7)=8HPLOT OF
      ITITLE(8)=8HCALCULAT
      ITITLE(9)=8HED ABSOR
      ITITLE(10)=8HBANCE VS
      ITITLE(11)=8H PH.
      DO 6 I=1,50
      HDR=1./(10.**PH)
      Y(I)=(D4+C*A*HDR*EP3+A*B*D2*HDR*HDR)/(1.+A*HDR+A*B*HDR*HDR)
      X(I)=PH
    6 PH=PH+.1
      CALL DRAW(50,X,Y,0,0,LABEL,ITITLE,0,0,0,0,1,1,8,8,0,LAST)
      STOP
      END
      END
```

Program input:

A= value of K_1

B= value of K_2

D2= A_2

D4= A_4

H= (H^+) and D= corresponding absorbance to be used in calculating a value of a3.

C= concentration of Pd.

APPENDIX V

Computer program for calculating tau versus kappa values for various percent reaction.

```
      PROGRAM RATIO
      DIMENSION CAPA(49),TOW(49,66)
      CAPA=1.1
      DEL=.3
      DO9 J=1,49
      DO8 I=1,66
      A=1.-2.*CAPA
      B=(1.-CAPA)*(2.-DEL)
      TOW= LOGF(A/B)
      DO7 K=1,50
      E=EXPF(-CAPA*TOW)
      IF(A/(B-E))30,30,7
30    TOW(J,I)=-1.0
      GO TO 8
 7    TOW=LOGF(A/(B-E))
      TOW(J,I)=TOW
 8    DEL=DEL+.02
      DEL=.3
      CAPA(J)=CAPA
 9    CAPA=CAPA+.1
      PRINT 11
11    FORMAT(3X4HCAPA6X5HTOW155X5HTOW165X5HTOW175X
     15HTOW185X5HTOW195X5HTOW205X5HTOW215X
     25HTOW225X5HTOW235X5HTOW245X5HTOW25///)
      PRINT 12,(CAPA(I),(TOW(I,J),J=1,11),I=1,49)
12    FORMAT(12F10.5)
      PRINT 13
13    FORMAT(3X4HCAPA6X5HTOW265X5HTOW275X5HTOW285X
     15HTOW295X5HTOW305X5HTOW315X5HTOW325X
     25HTOW335X5HTOW345X5HTOW355X5HTOW36///)
      PRINT 14,(CAPA(I),(TOW(I,J),J=12,22),I=1,49)
14    FORMAT(12F10.5)
      PRINT 15
15    FORMAT(3X4HCAPA6X5HTOW375X5HTOW385X5HTOW395X
     15HTOW435X5HTOW415X5HTOW425X5HTOW435X
     25HTOW445X5HTOW455X5HTOW465X5HTOW47///)
      PRINT 16,(CAPA(I),(TOW(I,J),J=23,33),I=1,49)
16    FORMAT(12F10.5)
      PRINT 17
17    FORMAT(3X4HCAPA6X5HTOW485X5HTOW495X5HTOW505X
     15HTOW515X5HTOW525X5HTOW535X5HTOW545X
     25HTOW555X5HTOW565X5HTOW575X5HTOW58///)
```

```
      PRINT 18,(CAPA(I),(TOW(I,J),J=34,44),I=1,49)
   18 FORMAT(12F10.5)
      PRINT 19
   19 FORMAT(3X4HCAPA6X5HTOW595X5HTOW605X5HTOW615X
     15HTOW625X5HTOW635X5HTOW645X5HTOW655X
     25HTOW665X5HTOW675X5HTOW685X5HTOW69///)
      PRINT 20,(CAPA(I),(TOW(I,J),J=45,55),I=1,49)
   20 FORMAT(12F10.5)
      PRINT 21
   21 FORMAT(3X4HCAPA6X5HTOW705X5HTOW715X5HTOW725X
     15HTOW735X5HTOW745X5HTOW755X5HTOW765X
     25HTOW775X5HTOW785X5HTOW795X5HTOW80///)
      PRINT 22,(CAPA(I),(TOW(I,J),J=56,66),I=1,49)
   22 FORMAT(12F10.5)
      STOP
      END
      END
```

APPENDIX VI

Computer program for calculating the logarithm of time ratios for various percent reaction.

```
      PROGRAM LOGRAT
      DIMENSION CAPA(50),TOW(50,7),RAT1(50,6),RAT2(50,5),
     1RAT3(50,4),RAT4(50,3),RAT5(50,2),RAT6(50)
      CAPA=1.1
      DEL=.2
      DO 9 J=1,50
      DO 8 I=1,7
      A=1.-2.*CAPA
      B=(1.-CAPA)*(2.-DEL)
      TOW=LOGF(A/B)
      DO 7 K=1,50
      E=EXPF(-CAPA*TOW)
    7 TOW=LOGF(A/(B-E))
      TOW(J,I)=TOW
    8 DEL=DEL+.2
      DEL=.2
      CAPA(J)=CAPA
    9 CAPA=CAPA+.1
      Z=.4342945
      DO 10 J=1,50
      DO 11 I=1,6
      RAT1(J,I)=Z*LOGF(TOW(J,7)/TOW(J,I))
   11 CONTINUE
   10 CONTINUE
      DO 12 J=1,50
      DO 13 I=1,5
      RAT2(J,I)=Z*LOGF(TOW(J,6)/TOW(J,I))
   13 CONTINUE
   12 CONTINUE
      DO 14 J=1,50
      DO 15 I=1,4
      RAT3(J,I)=Z*LOGF(TOW(J,5)/TOW(J,I))
   15 CONTINUE
   14 CONTINUE
      DO 16 J=1,50
      DO 17 I=1,3
      RAT4(J,I)=Z*LOGF(TOW(J,4)/TOW(J,I))
   17 CONTINUE
   16 CONTINUE
```

```
      DO 18 J=1,50
      DO 19 I=1,2
      RAT5(J,I)=Z*LOGF(TOW(J,3)/TOW(J,I))
   19 CONTINUE
   18 CONTINUE
      DO 20 J=1,50
   20 RAT6(J)=Z*LOGF(TOW(J,2)/TOW(J,1))
      PRINT 21
   21 FORMAT(3X4HCAPA6X5HT7/T15X5HT7/T25X5HT7/T35X
     15HT7/T45X5HT7/T55X5HT7/T65X5HT6/T15X5HT6/T25X
     25HT6/T35X5HT6/T45X5HT6/T5///)
      PRINT 22,(CAPA(J),RAT1(J,I),I=1,6),
     1(RAT2(J,K),K=1,5)J=1,50)
   22 FORMAT(12F10.6)
      PRINT 23
   23 FORMAT(3X4HCAPA6X5HT5/T15X5HT5/T25X5HT5/T35X
     15HT5/T45X5HT4/T15X5HT4/T25X5HT4/T35X5HT3/T15X
     25HT3/T25X5HT2/T1)
      PRINT 24,(CAPA(J),(RAT3(J,I)I=1,4),(RAT4(J,K),
     1K=1,3),(RAT5(J,M),M=1,2),RAT6(J),J=1,50)
   24 FORMAT(11F10.6)
      END
      END
```

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The following substitution reactions involving the square complexes of palladium (II) in aqueous HCl solution were studied by spectrophotometric and potentiometric methods:

$$Pd(NH_3)_4^{++} + H^+ + Cl^- \quad Pd(NH_3)_3Cl^+ + NH_4^+$$

$$Pd(NH_3)_3Cl^+ + H^+ + Cl^- \quad Pd(NH_3)_2Cl_2 + NH_4^+$$

Reaction rates, followed by (H^+) versus time measurements, suggest that parallel mechanisms obtain with one reaction involving the solvent as a nucleophilic reagent and a second reaction involving the incoming C^- reagent. Values of the equilibrium quotients for both reactions were calculated from absorbance and pH data. Several of the specific rate constants were calculated and a complete mechanism is proposed. Brief studies of the trans-effect in this system and of the cis-trans isomerism of $Pd(NH_3)_2Cl_2$ are included.

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